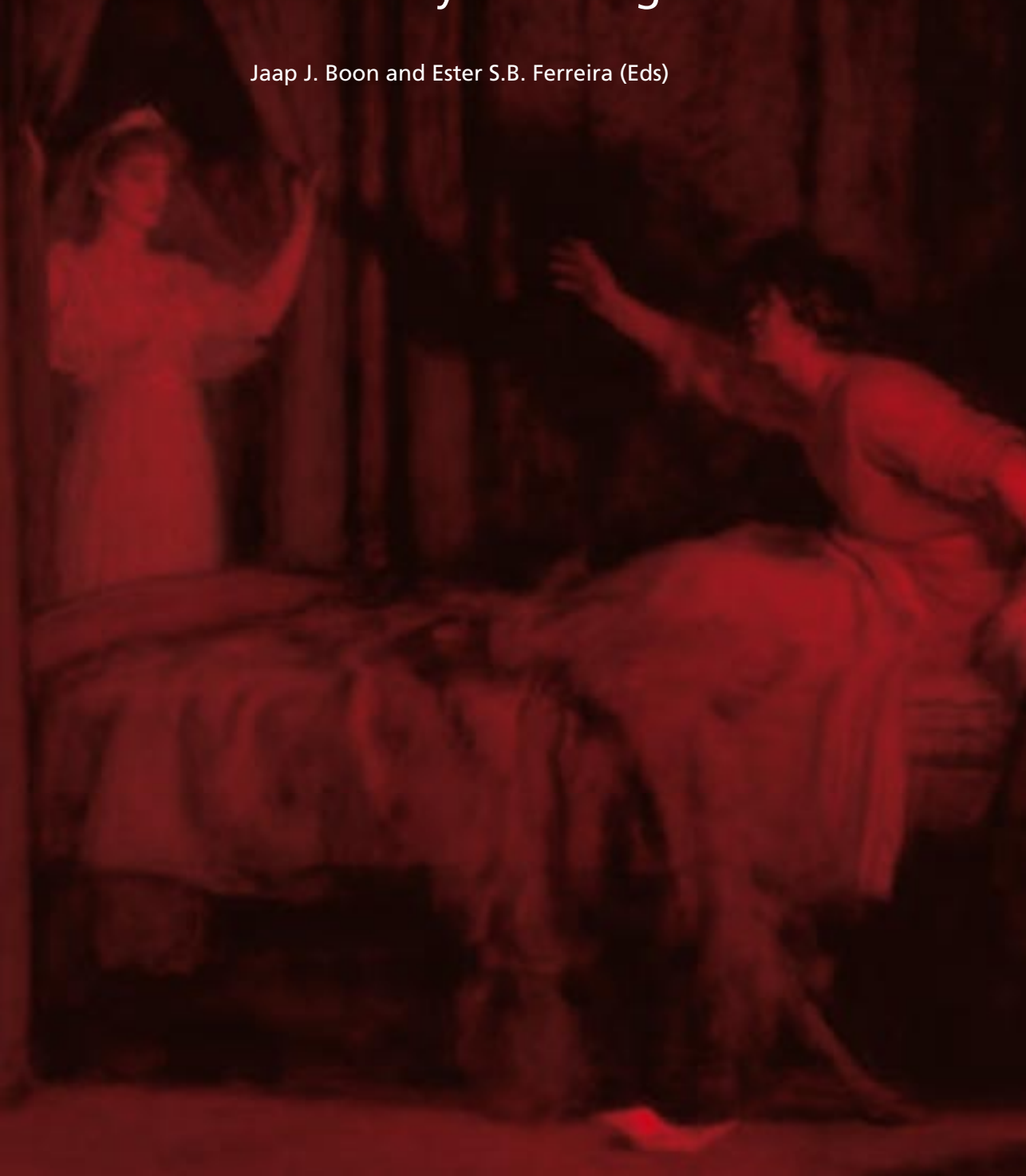


Reporting Highlights of the De Mayerne Programme

Jaap J. Boon and Ester S.B. Ferreira (Eds)



Colofon

Reporting Highlights of the De Mayerne Programme
Jaap J. Boon and Ester S.B. Ferreira (editors)
Published by NWO, The Hague, November 2006
ISBN 90-77875-14-X



Netherlands Organisation for Scientific Research

Netherlands Organisation for Scientific Research (NWO)
Divisions for Physical Sciences, Chemical Sciences and Humanities
P.O. Box 93460 2509 AL The Hague
The Netherlands
E-mail gbe@nwo.nl
Website www.nwo.nl/demayerne

Cover: Microscopic research on Allegory on time, Jacob Jordaens – Photo SRAL
Title page: Speak! Speak! (1895) by John Everett Millais (Tate). Inv. nr. N01584

Table of contents

Objectives of the De Mayerne Programme	7
J. Wadum	
The De Mayerne programme: breaking new grounds for art science and conservation in the 21st century	9
J. Wouters	
Surrealism in science: the difference between <i>analysis</i> and <i>analysis</i>	13
J.J. Boon	
Processes <i>inside</i> paintings that affect the picture: chemical changes at, near and underneath the paint surface	21
Michiel A. Verhoeven, L. Carlyle, J. Reedijk and J.G. Haasnoot	
Exploring the application of <i>solid-state</i> Nuclear Magnetic Resonance to the study of the deterioration of paintings	33
Y. Shimadzu and K.J. van den Berg	
On metal soap related colour and transparency changes in a 19th C painting by Millais	43
E.S.B. Ferreira, R. Morrison, K. Keune, and J.J. Boon	
Chemical Characterisation of thin intermediate layers: Case study of a sample from the 15th century painting <i>The Descent from the Cross</i> by Rogier van der Weyden	53
L. Carlyle	
Historically Accurate Reconstructions of Oil Painters' Materials: An overview of the Hart Project 2002-2005	63

Table of contents

E. Hendriks, S. Constantin, B. Marino Various approaches to Van Gogh technical studies; common grounds?	77
K.J. van den Berg, A. Burnstock, L. Carlyle, M. Clarke, E. Hendriks, R. Hoppenbrouwers, J. Kirby and I. Lanfear Fading of red lake paints after Vincent van Gogh – an interdisciplinary study involving three De Mayerne projects	89
A. van Grevenstein-Kruse Multidisciplinary research on the paintings ensemble in the Oranjezaal of the Royal Palace Huis ten Bosch	97
M. Clarke and L. Carlyle Recipe databases for historical oil painting materials: Winsor & Newton Archive	109
Appendixes	
List of publications	117
List of theses	119
List of communications	127

MOLART Reports

The MOLART reports summarise research results obtained in the course of the MOLART and De Mayerne Research Programmes supported by NWO (Netherlands Organisation for Scientific Research). Information about the MOLART reports can be obtained from Prof. Dr. J.J. Boon, FOM-Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands, boon@amolf.nl.

1. Molecular studies of fresh and aged triterpenoid varnishes, Gisela A. van der Doelen, 1999. ISBN 90-801704-3-7
2. A mathematical study on craquelure and other mechanical damage in paintings, Petri de Willigen, 1999. ISBN 90-407-1946-2
3. Solvent extractable components of oil paint films, Kenneth R. Sutherland, 2001. ISBN 90-801704-4-5
4. Molecular changes in egg tempera paint dosimeters as tools to monitor the museum environment, Oscar F. van den Brink, 2001. ISBN 90-801704-6-1
5. Discoloration in Renaissance and Baroque oil paintings, Margriet van Eikema Hommes, 2004. Archetype Publications, London.
6. Analytical chemical studies on traditional linseed oil paints, Jorrit D.J. van den Berg, 2002. ISBN 90-801704-7-X
7. Microspectroscopic analysis of traditional oil paint, Jaap van der Weerd, 2002. ISBN 90-801704-8-8
8. Laser Desorption Mass Spectrometric Studies of Artists' Organic Pigments, Nicolas Wyplosz, 2003. ISBN 90-77209-02-6
9. Molecular studies of Asphalt, Mummy and Kassel earth pigments: their characterisation, identification and effect on the drying of traditional oil paint, Georgiana M. Languri, 2004. ISBN 90-77209-07-7
10. Analysis of diterpenoid resins and polymers in paint media and varnishes; with an attached atlas of mass spectra, Klaas Jan van den Berg (forthcoming).
11. Binding medium, pigments and metal soaps characterised and localised in paint cross-sections, Katrien Keune, 2005. ISBN 90-77209-10-7
12. Paints quantified: image analytical studies of preparatory grounds used by Van Gogh, Beatrice Marino, 2006. ISBN-10: 90-77209-19-0 and ISBN-13: 978-90-77209-19-6
13. Reporting Highlights of the De Mayerne Programme, Jaap J. Boon and Ester S.B. Ferreira (Eds) ISBN 90-77875-14-X

Published MOLART reports can be ordered from Archetype Publications, 6 Fitzroy Square, London W1T 5HJ, England, Tel: +44 207 380 0800 Fax: +44 207 380 0500, info@archetype.co.uk.

	Project cluster	Co-ordinating PI
P1:	Comparative studies of the paintings in the Oranjezaal	Prof. A. van Grevenstein-Kruse
P2:	Painting technique and the studio practice in the Dutch Golden Age	Dr. A. Wallert
P3:	Co-ordination chemical changes in oil paintings	Dr. J. Haasnoot
P4:	Imaging microscopy of paintings cross sections	Prof. Dr. J.J. Boon
P5:	Reconstructing 17 th and 19 th C oil paint	Dr. L. Carlyle
P6:	Painting media of Van Gogh	E. Hendriks
P7:	Effects of cleaning	Prof. A. van Grevenstein-Kruse
P8:	High resolution IRR studies paintings and miniatures	Prof. Dr. M. Faries
P9:	Fate of proteins in works of art	Prof. Dr. J.J. Boon
P10:	The chemical atmosphere around art	Prof. Dr. C. Elsevier
P11:	Surface studies of paintings by UV-VIS	Drs. IJ. Hummelen

Table 1. Project clusters developed for the De Mayerne Programme with their managing principal coordinating investigators (PI).

Objectives of the De Mayerne Programme

The programme of the Netherlands Organisation for Scientific Research (NWO) on *Molecular Studies in Conservation and Technical Studies in Art History* was named after Sir Theodore Turquet de Mayerne who studied medicine in Montpellier and Paris. He moved to London in 1611 to become principal physician to James I. During his stay at the English court he carried out research on technical aspects of painting. He performed chemical experiments, leading to the discovery of a purple pigment for enamel painting. The results of his studies are contained in his manuscript *Pictoria sculptoria et quae subalternarum artium* (London BL Sloane MS 2052). Although this manuscript surfaced in the 19th C, De Mayerne can be considered as the first conservation scientist and his manuscript is still used as one of the main sources on 17th century painting techniques.

The ambition of De Mayerne programme was to further develop and extend the knowledge and insights on molecular and paint technical structure of paintings obtained in the NWO Priority Programme MOLART -- *Molecular Aspects of Ageing in Art* (1995 - 2001). MOLART acted as a catalyst to bring together members of the research community on technical studies in art history, molecular sciences and conservation in the Netherlands and in this way revitalised an older tradition of fundamental research in art. It was a recognisance programme on molecular studies of art objects especially paintings. It achieved an increased awareness of the potential of the molecular approach to understand complex phenomena caused by internal and external factors that change the quality of paintings.

The mission of the De Mayerne programme was to further stimulate the establishment of a strong cross-disciplinary central research programme on technical studies in art history and molecular conservation studies of art objects in the Netherlands. It also intended to encourage the participation of the natural sciences in the analysis and solution of art technical and conservation problems in paintings and related art objects. It furthermore to promote studies in studio practices of painters, in ageing processes in works of art and the effects of conservation practices, all research topics of great importance for the preservation of our cultural heritage. A close collaboration and feed-back from Dutch museums was regarded as essential for the success of the De Mayerne programme, an engagement that furthermore would guarantee the broad relevance of the mission.

Various multidisciplinary research projects (Table 1) were developed that grouped research topics together in project clusters in which research groups from different

institutions were to collaborate. These project clusters were also the anchors for the general call for proposals. In competition, project cluster proposals were selected to be financed by the programme. Proposals were evaluated by an international group of referees, graded and presented to the De Mayerne Programme Committee¹. Projects within the clusters P1, P3, P4, P5, and P6 (table 1) received funding in the first round. In a second round, projects were supported in the clusters P3, P5, P8 and a proposal outside these clusters on transparency changes in 19th C paintings. A description of these projects can be found on the website www.nwo.nl/demayerne. The projects benefited greatly from the collaboration with the Van Gogh Museum research team, the Royal Cabinet of Paintings The Mauritshuis and the Limburg Conservation Studio (SRAL), which coordinated the Oranjezaal research consortium. The Programme Committee organised an opening symposium, a mid term evaluation and the final symposium on 17 November 2006, in order to publicly present the research plans and results in the course of the Programme.

Via the supported projects, the programme has supported in part the PhD research work of Katrien Keune, Beatrice Marino, Ella Hendriks, Annelies van Loon, Maartje Witlox, Yoshiko Shimadzu and Frank Hoogland, who benefited from the collaborative spirit and facilities provided by the participating research institutions like AMOLF, ICN, University of Leiden, SRAL and several museums. Some of these dissertations are still underway. A very large body of research work produced by the Oranjezaal research team will be published in a special publication devoted to this unique paintings ensemble. The present book presents highlights from the programme in the form of research papers and critical progress reports. The lists of theses, publications and presentations give an account of the output.

Jaap J. Boon and Ester S.B. Ferreira (editors)

¹ The programme committee consisted of, Chair: prof. dr. J.P. Filedt Kok (Rijksmuseum Amsterdam) and Members: dr. D. Bomford (National Gallery London), prof.dr. E.J. Sluifster (Institute for Atomic and Molecular Physics), prof.dr. E. van Uitert (University of Amsterdam), dr. J. Wouters (Royal Institute for the Study and Conservation of Belgium's Artistic Heritage in Bruxelles), dr. R.L.J. Zsom (University of Amsterdam, Institute for Molecular Chemistry) and former member prof.dr. J.T.M. Walraven (Institute for Atomic and Molecular Physics). Secretariat: Dr. N.J. Kos and drs. G.E. Thoen (NWO Physical Sciences Council, The Hague).

The De Mayerne programme: breaking new grounds for art science and conservation in the 21st century

When the Dutch Delta-plan for Cultural Heritage Protection² was inaugurated in the early 1990's nobody would have thought that The Netherlands was to become later world renowned not only for its focus on preventive and active conservation of the cultural heritage, but also for an innovative analytical approach and development of expertise in understanding aging and molecular changes in art works.

The MOLART project and its continuation in The De Mayerne Project will go down in history as the best investment in the protection of cultural heritage ever offered by the Netherlands Organisation for Scientific Research (NWO) by aiming at understanding the degradation processes in works of art. One outcome of this grand project is the numerous books, publications and symposium papers. Another outcome has been a large number of graduate students that received a dissertation and many young restorers who were exposed to innovative approaches in painting studies. The knowledge transfer is beginning to bear fruit, and a continuation of the research would seem essential in order to nourish not only the instrumental and ground breaking research but also to enable the results to become fully embedded in applied conservation-restoration practice. As with all research the knowledge gained in the initial phases of MOLART and during the De Mayerne programme will have to be tried first in practice, be evaluated and even re-visited in new analytical environments. Subsequently, what has been confirmed can be applied in the conservation studio. This process is underway and will, if the research is continued in one form or the other, be of essential value to the future understanding and keeping of our cultural heritage.

¹ Statens Museum for Kunst, Sølvgade 48-50, 1307 Copenhagen K, Denmark, j.wadum@smk.dk

² Nota Deltaplan voor cultuurbehoud by the Dutch ministry of Welfare, Health and Culture (Ministerie van WVC), 1992.

For generations a variety of sources and painters manuals have been the natural starting point for understanding the paintings and art object, their appearance and/or degradation. So when Sir Theodore De Mayerne himself in the 1620's recommends artists not to use a binding medium rich mixture of linseed oil in combination with blue pigments in order to not create a long-term discolouration of the blue into a more murky blue-green substance. His recommendation was based on common practice and painters' experience. Such observations made by artists were continuously recorded throughout the centuries and are important starting points for conservation science. On the other hand, Philips Angel stated in 1642: "no painting was assured to last for ever and that they will change over time as nothing but the love of God will stay unchanged". He continued that in his opinion paintings might last a few hundred years - which would be enough.³

Today, as we are excited to still have objects from his period and before, man remains continuously impressed, enriched and moved by their visual impact. Unsurprisingly, the images have changed some just slightly or discretely while some maybe even nourishing a 19th century romantic notion about aged artworks and their patina. Other objects have changed dramatically and show areas severely darkened, blanched, or otherwise with disturbed or altered surfaces.

Although having examined and treated numerous paintings over the past centuries conservator-restorers have not always had an understanding of many of the phenomena appearing under their able hands. As Jaap Boon writes elsewhere in this book, the tiny holes and protrusions earlier described as the result of an 18th century nearby fire affecting Rembrandt's Anatomy Lesson of Dr Nicolaes Tulp (The Hague, Mauritshuis) became a starting point for an exiting new path of understanding of molecular aging phenomena in oil paint. In 1996 before embarking on the treatment of the painting the conservators were anxious that the many tiny holes all over the surface, some with whitish protrusions, could have been caused by an earlier treatment with copaiba balsam. This method, extensively used in the late 19th and up into the 20th century to reform and regenerate aged varnishes, is much better understood thanks to molecular analysis done by an interdisciplinary team of conservators and conservation scientists. Advanced analysis of paint and lining materials from the Anatomy Lesson fortunately found no residues of copaiba balsam. Did this mean that the unambiguous records stating extensive use of copaiba balsam after all were not reliable? Was the content of the bottle with copaiba balsam substituted by an etheric oil that we could not identify? Or was the use of the balsam not at all the reason for the tiny holes?

Extensive interdisciplinary research could be initiated thanks to the creation of an Open Laboratory agreement between Boon from AMOLF and the current author and colleagues at the Mauritshuis. This collaborative effort resulted not only the identification of what was actually happening in the painting i.e. where metal soap aggregates had developed inside the paint layers that later expanded and moved their way out through the surface as protrusions, but also that a safe restoration could be undertaken. The research cleared the way for a treatment that otherwise

was posing a high degree of uncertainty and potential risk. Shortly afterwards the awareness of the protrusion phenomenon spread to museums all over the world, and no conservation studio that is treating paintings can be unaware of these phenomena now, their complex account and the challenges to further proceed with a conservation treatment of a painting featuring evidence of protrusions.

In the same way much research by the De Mayerne team has revealed new insights into the understanding of the formation of blanching in the form of crust forming on the surface of paint layers. If one without the knowledge of the De Mayerne research would attempt to remove this blanching either by cleaning or reforming with solvents an approach that certainly in the past has been attempted in many studios-, damage to the original paint surface would easily be the result. Degradation of the paint layer caused by the migration of lead soaps from lower layers up to the surface where they further undergo a reaction with other elements from the paint and from the environment is therefore important information to the bench workers in the museum studios.

So is the multitude of results from the multifaceted research of the huge paintings in the Oranjezaal of the Royal Palace Huis ten Bosch. This investigation has fostered exiting new insights into seventeenth century artworks, their making and meaning. It is fascinating to acknowledge that materials identification and archival studies can be fused into understanding the train of thoughts of the creative minds of the artists involved. As I pointed out during participation of the preliminary investigation and examination of the Oranjezaal in 1997, it would be vital to include Pieter de Grebbers Rules (Regulen) from 1649 in the interpretation, something that now has been extensively discussed in relation to the ensemble.⁴ Understanding the original materials and their behaviour during aging also offers a unique new insight into how conservation and restoration materials from the recent past may have altered not only the appearance but also the molecular structures of the original. Wax-linings introduced as a Dutch 'invention' in the 19th century and extensively used all over Northern Europe have taken their toll on many paintings, something now powerfully documented. This research adds considerably to the knowledge of practising conservator-restorers.

Reconstructing paint after an accurate approach of interpreting recipes has further broadened our understanding of the rheology and performance of maturing paint. Databases and phenomenological atlases on artists' material and analytical results of known and documented pigments and binding media would broaden our understanding even better and it is hoped that this research and documentation will be carried further in the years to come.

³ Philips Angel, *Lof der Schilder-konst*, Leiden 1642, p. xx, '...verseeckert sijn van altijd te duyren: of sy sijn de veranderlicheynt onderworpen, niets en behouter een onbeweeghlicke een blyvende Godt, ook soo kunnen de Schilderyen eenige honderde jaren duyren, het welke ghenoech is...'

⁴ ArtMatters Netherlands Technical Studies in Art 3, Waanders Zwolle 2005, 20-36.

Also in modern or contemporary artworks the molecular chains are in a continued state of alteration. It is of paramount importance to continue the research initiated by the De Mayerne programme in order to generate further knowledge and know-how about these transformations. The darkening or colour transparency of paintings by 19th century painters such as for example those of the school of Barbizon, the fading of lakes in paintings by Van Gogh and artists from his and later periods are other examples. Painter's manuals are useful; however, when artists in the 20th century became even less craftsman-like trained, the abundance of non-compatible materials used and piled on top of each other will evidently create huge problems for the generations aiming at keeping these objects.

We have now identified a number of relevant issues in aging paint and related materials that were not evident earlier due to the lack of molecular research such as carried out by the De Mayerne project members. Future generations will be offered a better opportunity to understand what went wrong in the artworks, knowing what can be accomplished by means of new and ground breaking science and innovative instrumentation operated by an ever increasing new generation of conservation and art scientists⁵. Obviously with more in depth research the complexity of the materials examined and the interpretation of the multivarious results makes the explanation more multifaceted and demanding. It will, however, offer the academically trained conservator-restorer an unprecedented opportunity to act and react adequately when working on preservation of our common heritage.

In publications for the professional field of heritage managers, scientists and conservator-restorers such as those in the Pre-prints of the ICOM Committee for Conservation, the IIC Post-prints and many other publications, colleagues around the globe have been made aware of the issues studied and of proposals for an understanding of the matter and the consequences during treatment. This again has prompted new observations and research elsewhere and a fruitful dialogue is rapidly growing about the essential issue behind the De Mayerne project: molecular aspects aging of paint. By a continued multidisciplinary research and adequate knowledge transfer will it become possible to create scenarios for treatments that may prolong the visual impact of our artworks far beyond any expectation of seventeenth century art lover Philips Angel.

No recent ambitious and interdisciplinary research project within the keeping of our past cultural heritage for the future has come so close to reach its objective as has The MOLART and De Mayerne projects. A continuation under one or the other form is therefore strongly recommended.

⁵ See the Amolf-NWO MOLART PhD dissertation publications 1-12.

Surrealism in science: the difference between *analysis* and analysis

Abstract

The term "*analysis*" should not be used without any further specification, when dealing with art in a multidisciplinary study group. Many terms dealing with analysis, even those that aim to be descriptive and explanatory, may generate confusion and reservations. Among the most notable of such terms are destructiveness, invasiveness, representativeness and resolution. In the De Mayerne research programme was decided to strive for minimal intervention while aiming for producing highly detailed results. This has led to the identification of technological features and ageing processes at the molecular level, thanks to the application of spearhead technologies, sometimes totally innovative in the field, and to sustaining archival studies and productions of historically accurate reconstructions. This holistic approach was discussed and accepted in the multidisciplinary De Mayerne research consortium.

The network's philosophy, approach and outcomes may be used to propose a new framework of criteria to help estimating the appropriateness of analysis of art: degree of intervention, preferably specified in a time-resolved manner, usefulness and innovation. This may solve confusion around terms such as invasiveness and destructiveness and may better show the integration, but also the specific demands, services and objectives, of fundamental and applied research when analysing art.

¹ Koninklijk Instituut voor het Kunstpatrimonium (KIK / IRPA), Jubelpark 1, B-1000 Brussels, Belgium, jan.wouters@kikirpa.be

Introduction

The multidisciplinary of approaches needed to investigate and understand the interactivity of the manufacture, ageing and best conservation practice of paintings is beyond any doubt. However, providing the supporting objective-tailored human, financial and technical resources to respond to that need, often seems problematic if not impossible, unless when programmed and managed within multinationally constructed and supported consortiums.

The De Mayerne programme, together with its predecessor MOLART, has provided national research funding for cross-boundary collaborations for a total duration of around ten years. This open-sight policy has certainly catalysed triggering of interest of the international professional community, not only in the scientific results obtained and in their potential impact on paintings conservation practice, but also in the diagnostic and conservation-supporting analytical protocols which were routinely applied as well as newly developed.

Such analytical protocols involve ever-increasing sophistication of sample preparation procedures, instrumentation and post-run data treatment. They have generated over time new terms, abbreviations and acronyms, which constitute a nearly new language. Moreover, when browsing the relevant literature, it seems that terminology on scientific analysis, used within the broader cultural heritage framework, is often confusing, contradictory and incomplete (Cassar and Degrygn 2005). All this may create an alienating effect on those professionals who are not familiar with the inherent terminology and evaluation processes, yet are closely involved in the multidisciplinary approach which must lead to the preservation of cultural heritage. There is no doubt that this may generate reservations when the appropriateness, usefulness and/or effectiveness of "analysis" is discussed.

The aim of this contribution to the proceedings of the De Mayerne Final Symposium is to discuss in human language, and based on the achievements of the De Mayerne research programme, major variables associated with the simple term "analysis", as well as to search for new terms which may reflect the quality of analysis in responding to a given need or request, in a better way than those used today.

Destructiveness

The withdrawal of a sample from an object of art or culture inevitably implies some kind of mutilation, even when executed in an inconspicuous area or when dealing with minute samples. Such handling is therefore called destructive to the object. On the other hand, there are analytical techniques available which may be applied directly to the object, without the removal of a sample being required. These techniques are often referred to as non-destructive and they are almost exclusively applied to inorganic materials in art (Demortier and Adriaens 2000). However, from a scientific point of view, any interaction between a material and an analytical vehicle, such as a focused beam of particles or electromagnetic radiation, is unlikely to leave that material unaltered after the interaction. The key feature in this discussion is the way in which is "looked" for damage. Obviously, the least critical position may be expected from evaluations of damage by the naked eye (there is no damage if

it cannot be “seen”), the most critical one from data generated at the molecular level by relevant spectroscopic techniques (there is no damage if the molecular compositional array at the spot of measurement has not changed beyond experimental deviations or beyond a preset level of tolerance). Intermediate evaluation levels may be magnifying glasses, optical and electronic microscopes. Sometimes, techniques applied directly to the object are called non-invasive. While being correct in terms of non-sampling, the qualification may be misleading in terms of destructiveness for the reasons outlined higher. Moreover, the usefulness of non-invasive approaches may be hampered by their rather surface oriented character and relatively high atomic mass detection threshold. The term “surface” then refers to that part of the whole multilayered construction which is transparent to the interacting beam, taking into account possible complications caused by quenching effects. However, when dealing with paintings, it was specified on several occasions that perception of damage was caused by alterations measured in deeper layers (Boon 2006; Shimadzu and van den Berg 2006).

In many cases, the complex combinations of inorganic and organic materials in objects of art and culture will require the removal of samples and the establishment of hyphenated analytical protocols. The latter should involve groups of techniques that respect a gradient of increasing destructiveness, ranging from observational (e.g. microscopy), over spectroscopic (e.g. Raman) to chromatographic (e.g. high performance liquid chromatography). Alternatively should be looked for analytical techniques which may be universally applicable to, both, organic and inorganic materials and which involve overlaying of selected mappings and anticipating problems associated with the a-specific atomic composition of organic materials. Chemical imaging using mainly secondary ion mass spectrometry (SIMS), but also eventually combined in overlay with mappings obtained by Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy linked to energy-dispersive x-ray detection (SEM-EDX) and (visible) light microscopy (LM), has been successfully applied in the De Mayerne programme (Boon 2006). Hence, the balance between quality and usefulness of analytical output, and degree of mutilation, was demonstrably highly positive!

Another debate that may interfere with observations on destructiveness and with the balance between quality of analytical output and mutilation is the one dealing with terms such as simple tests and sophisticated analyses. The former are thought of as evaluation tests, developed by scientists to meet the needs of people directly involved with the conservation of objects. The emphasis lies on the simple and safe execution of a measurement for performing a condition evaluation on objects or samples to allow visual or, at best, microscopic observations of the test result. The latter cover analyses, executed with instruments displaying ever-increasing performance in terms of sensitivity, resolution and diagnostic power, leading to lower sample consumption and higher detail of data. It is surprising to see that simple tests may be more readily accepted by conservators, even when such tests involve a higher risk for more substantial damage as compared to a sophisticated analytical protocol to be executed in a dedicated laboratory on a micro sample (Wouters 2003).

Representativeness

From the moment of its creation, an object starts to age. Ageing as such is a process resulting from changes over time, brought about as a consequence of production technology, environmental conditions, handling and repair. In most but not all cases is ageing associated with damage (Calver 2006). When the condition of such an aged or damaged historic(al) object or of one or more of its constituent materials has to be evaluated before deciding to conservation treatment, analysis has to be executed, and representative parameters for the description of damage have to be developed and interpreted. Since the object itself is the only product available for such an evaluation, the destructiveness of sampling and of the analytical approach will be important parameters to take into account.

According to the discussion on destructiveness given higher, measurements will have to be performed using microsamples or non invasive techniques, the latter with the known limitations. In the former case, analysis will often be performed using nanobeams (e.g. SEM-EDX; Raman microscopy). Taking into account the complex composition of artifacts such as paintings, as well as the high level of heterogeneity even when considering one single paint layer, it must be clear that a microsample and an analytical result generated from a micro spot don't represent but themselves. An improvement of damage evaluation and of the identification of processes that provoke damage will only be possible when considering multiple sampling and/or high resolution mapping and imaging techniques. Such multiple sampling was considered of prominent importance for the statistical comparison of analytical results so as to lead to the ultimate establishment of the painting technologies, the ageing pathways and the associated conservation issues of the 17th century paintings of the Oranjezaal (van Grevenstein-Kruse 2006).

The normally more considerable diameters of beams used in the non invasive approaches are advantageous in terms of averaging and, hence, increased representativeness. But they may miss phenomena vital to explain technology and /or damage, hence to suggesting conservations measures, due to the inherent lack of analytical resolution, both in the plane and in the depth of the artefact.

References: archival studies and reconstructions

Many archival sources have been explored to assist revealing ancient manufacturing technologies, but many others are still waiting to be studied, even probably to be discovered. The importance and need to research archival information is emphasized by the recent creation of a working group, specifically dedicated to "Art Technological Source Research" within ICOM-CC (Anonymous 2006; Clarke et al. 2005).

The way in which archival research can be usefully incorporated in a larger framework of study of the composition and ageing of paint is illustrated by the establishment of recipe databases for historical oil painting materials, based on the Winsor & Newton archives. Technical data in this archive was made available in a database format and could be queried to help interpreting the data obtained on historic samples (Clarke and Carlyle, 2006).

One step further is using the archival data, once transcribed in present day language

and units of measure, to produce reconstructions in the laboratory. Such tangible reconstructions, when kept together with information on historical sources, on the ways these sources were interpreted, and on the provenance and use of present-day materials and products purchased to make the reconstructions, will constitute a reference collection, preferably shared over several institutions. Such a reference collection shall serve the needs of present and future research, and shall contribute to lowering the mutilation of precious artifacts, yet to improving the quality of the analytical outcome (Carlyle 2006).

A search for documentary and archival information relating to the manufacture and retail of artist materials in the late 19th century in France, combined to the creation of relevant reconstructions and quantitative characterisations of colour, particles, elements and minerals, has moved forward the understanding of technique and chronology of Van Gogh's paintings of his Paris period (Hendriks et al. 2006).

Reconstructions may also be used to estimate any future proliferation of damage to be expected as a function of environmental conditions for instance (van den Berg et al. 2006). Reconstructions may be used as such or may give way to the creation of a damage monitoring system, possibly sensitivity-enhanced when based on an assembly of the most sensitive elements of the reconstruction in the monitor or sensor. This then allows for, both, a quick response to a jeopardizing condition and a more liberal position with respect to sample consumption and analytical approach in terms of destructiveness, since the object is not directly involved anymore. Since alertness is then the most important feature, simplicity of approach prevails (Bacci et al. 2005).

Discussion of new criteria to determine the appropriateness of analysis in art

The term "analysis" is a flag that covers many loads, even when accompanied by adjectives or descriptions trying to case-specify the exact meaning of the word. The multidisciplinary of research groups dealing with cultural heritage issues further complicates the creation and use of mutually understandable terms. Key controversies may arise with respect to the destructiveness of an analytical protocol, to reservations towards the application of spearhead technologies when opposed to the availability of "simple tests", to the anticipation of usefulness of the analytical data to be produced and to the different needs of parties involved.

"Shouldn't we step down from the often confusing terms that accompany 'analysis' when discussing the ways in which revealing the manufacturing technology, ageing and damage of artifacts should be addressed?" is a rhetorical question, the answer to which should extend beyond the suspected "yes!".

In one of the contributions to the present proceedings was used the term "minimal intervention" when addressing the molecular approach to the analysis of the composition and condition of paint (Boon 2006). The term "intervention" is interesting, because it avoids controversial terms such as destructiveness and invasiveness.

The degree of intervention might be described at three levels, such as molecular (low change), microscopic (medium change) or visual (high change). This would imply for instance that the withdrawal of a microscopic sample or the generation of a

permanently discoloured microspot (as a consequence of prolonged remote radiation) do reflect exactly the same degree of intervention, whereas the microsampling should have been called invasive, the radiation non-invasive but apparently destructive in older terms. Moreover, the degree of intervention and its discussion should be time-related. Indeed, discolouration caused by radiation in a focused beam may be either permanent or limited in time. This may lead to calling a degree of intervention high/medium (permanent visual/microscopic observation of change) or low (initial visual/microscopic observation of change, later only molecular change), although both measurements were executed in old non-invasive terms.

However, the degree of intervention does not explain at all why analysis is proposed, requested or executed, by whichever party. More information is needed on the expectations of the requestor in terms of how analytical results will be used. Such information may refer to usefulness and innovation.

Usefulness of intervention should be considered related to giving direct support to learning production technology, to making damage assessment and to determining conservation practice. Such data will probably be generated and interpreted with the help of available personal or institutional or generally accessible approaches and databases.

Innovation may be formulated in terms of progress beyond the state of the art. Initially, innovation may not critically take into account the degree of intervention (Verhoeven et al. 2006) or usefulness (Della Gatta et al. 2005) of analysis executed according to the newly developed approach. But it is wishful that a high level of innovation shall create data, insights and experience which, on their turn, will improve usefulness and probably even lower the degree of intervention on the longer term.

The combination of usefulness and innovation touches the grey zone between conservation science and fundamental research. Possibly, both should be merged into "Art Science", aiming for as high as possible levels of usefulness and innovation with a minimal degree of intervention when suggesting analysis. Art Science should then not only cover natural science but also the scientific approaches of conservation, history, art history, technology and mathematics.

Level of intervention, usefulness and innovation may be rightfully used and combined to estimate the balance between the degree or level of intervention and the analytical outcome. And it will be exactly this balance which must be discussed by all parties involved to lead to the selection of the, in all terms, most appropriate analytical approach. Increased transparency by using the terms degree of intervention, usefulness and innovation in a descriptive way to discuss scientific analysis in a multidisciplinary environment may improve source's credibility, receiver's attention and decision's quality (Henderson 2005).

Conclusion

Preserving the momentary integrity of a work of art and intervening with that same work of art to assess its production technology and its compositional changes, often referred to as damage, as well as to formulate decisions on how to secure its state of conservation, do often generate conflictuous points of view. Nomenclatures,

abbreviations, acronyms and their interpretations are specific for each of the parties involved in art science. Some of them may be misleading if not suitably commented. The De Mayerne programme as a whole, building upon the former MOLART research, has provided ample opportunity to network between disciplines. This has created a forum wherein analysis of works of art could be openly discussed in terms of objectives (e.g. the causes of darkening), protocols (e.g. representative analyses of over 500 cross-sections from the Oranjezaal paintings), usefulness of innovative tools (e.g. solid state NMR) and sustaining activities (e.g. archival research and historically accurate paint reconstructions). Implicitly, this network has created a position towards analysis in art science, the subtlety of which stretches far beyond the classical and much too simple destructiveness/invasiveness dilemma. Analyses of historical materials have almost exclusively been performed on samples, withdrawn from objects. But the application of spearhead technologies with high spatial and molecular resolving power, also for organic materials, has generated highly detailed results on microsamples.

The network's philosophy, approach and outcomes may be used to propose a new framework of criteria to help estimating the appropriateness of analysis of art: degree of intervention, to classify probable damage to the object as low (molecular), medium (microscopic) or high (visual), preferably commented in a time-resolved way to cope with eventual long-term effects of the intervention; usefulness, to interpret the result of analysis for technological research, damage assessment and conservation treatment, probably relying upon existing reference data and practices; and innovation to describe the potential of an analytical approach in terms of progress beyond the state of the art. This framework of criteria may solve the confusion around terms such as invasiveness and destructiveness and may better show not only the specific demands, but also the integration of fundamental and applied science when analysing art.

Hopefully, these new criteria shall be of help when discussing analysis for measuring the effect of conservation treatments on momentary damage and future ageing processes.

References

- Boon J.J., Ferreira E.S.B., Keune K. (2005). *Imaging analytical studies of Old Master paints using FTIR, SIMS and SEMEDX of embedded paint cross-sections. Microscopy and Micro-analysis*, 11, p. 1370-1371.
- Anonymous (2006). *Newsletter of the ICOM-CC Working group on Art Technological Source Research, Volume 2, number 1 (June). Unpublished. See also www.icom-cc.com.museum*
- Bacci M., Cucci C., Dupont A.-L., Lavédrine B., Loisel C., Gerlajc S., Roemich H., Martin G. (2005). Light-Check ®, new disposable indicators for monitoring lighting conditions in museums. In: *Preprints of the 14th Triennial Meeting of the ICOM Committee for Conservation* (Verger I. ed.). James & James, London. p. 569-573.
- Boon J.J. (2006). Processes inside paintings that affect the picture: chemical changes at, near and underneath the paint surface. In: *Reporting Highlights of the De Mayerne Programme*, (Jaap J. Boon and Esters S.B. Ferrera), Den Haag, p. 21-32
- Calver A. (2006). 'Yes we can help you do that': Communication a positive conservation message. In: *Newsletter of the ICOM-CC Task Force on Public Engagement in Conservation*. July 2006, p. 8-17. Unpublished. See also www.icom-cc.com.museum
- Carlyle L. (2006). Historically accurate reconstructions of oil painters' materials : an overview of the Hart project 2002-2005. In: *Reporting Highlights of the De Mayerne Programme*, (Jaap J. Boon and Esters S.B. Ferrera), Den Haag, p. 63-76
- Cassar J., Degriigny C. (2005). The philosophy of the workshop. In: *Benefits of non-destructive analytical techniques for conservation* (Adriaens A., Degriigny C. and Cassar J., eds.), COST Office, Luxembourg, p. 9-12.
- Clarke M., Townsend J.H., Stijnman A., eds. (2005). *Art of the Past ; Sources and Reconstructions*. Proceedings of the first symposium of the Art Technological Source Study group; Archetype Publications Ltd.
- Clarke M. and Carlyle L. (2006). Recipe databases for historical oil painting materials : Winsor & Newton Archive. In: *Reporting Highlights of the De Mayerne Programme*, (Jaap J. Boon and Esters S.B. Ferrera), Den Haag, p. 109-114
- Della Gatta C., Badea E., Masic A., Usacheva T., Benedetto S. and Braghieri A. (2005). Environmental ageing of historical parchments: a DSC, SEM and unilateral NMR study of old bookbindings from the Historical Archives of the City of Turin. In: *Improved Damage Assessment of Parchment*, School of Conservation, The Royal Danish Academy of Fine Arts, Copenhagen, p. 41-42.
- Demortier G., Adriaens A. eds. (2000). Ion beam study of art and archaeological objects, European Commission, Luxembourg.
- Henderson J. (2005). *Influence: The Impact of Language, Credibility and Gender. The Conservator*, 29, p. 63-72.
- Hendriks E., Constantin S., Marino B. (2006). Various approaches to Van Gogh technical studies; common grounds ? In: *Reporting Highlights of the De Mayerne Programme*, (Jaap J. Boon and Esters S.B. Ferrera), Den Haag, p. 77-88
- Shimadzu Y., van den Berg K. J. (2006). On Colour and Transparency changes in 19th Century paintings. In: *Reporting Highlights of the De Mayerne Programme*, (Jaap J. Boon and Esters S.B. Ferrera), Den Haag, p. 43-52
- van de Berg K.J., Burnstock A., Carlyle L., Clarke M., Hendriks E., Hoppenbrouwers R., Kirby J., Lanfeer I. (2006). *Fading of red lake paints after Vincent van Gogh – an interdisciplinary study involving three De Mayerne projects*. In: *Reporting Highlights of the De Mayerne Programme*, (Jaap J. Boon and Esters S.B. Ferrera), Den Haag, p. 89-96
- Verhoeven M.A., Carlyle L., Reedijk J., Haasnoot J.J. (2006). *Exploring the application of solid-state Nuclear Magnetic Resonance to the study of the deterioration of paintings*. In: *Reporting Highlights of the De Mayerne Programme*, (Jaap J. Boon and Esters S.B. Ferrera), Den Haag, p. 32-42
- Wouters J. (2003). *Damage assessment approaches for organic materials in art: simple tests or sophisticated analyses ? In: Proceedings of the 5th EC Conference, 'Cultural heritage Research: a Pan-European Challenge'* (Kozlowsky R., ed.) European Communities, Luxembourg, p. 61-66.

Processes *inside* paintings that affect the picture: chemical changes *at, near* and *underneath* the paint surface

IMAGING & STRUCTURAL ANALYSIS OF MEDIA AND PIGMENTS IN CROSS SECTIONS OF PAINTINGS (MOLMAP)

Abstract

The nature of the surface of the painted picture is determined to a large extent by chemical and physical processes underneath the surface of the paint. The binding medium changes from a chemically drying viscous mass of cross linking polyunsaturated triglycerides "the oil" via slow hydrolytic processes to a metal bound ionomer. This network system in turn appears to be vulnerable to further environmental attack especially by acidification that is postulated to disrupt the ionic structure. As a result monocarboxylic fatty acids can be mobilized and reorganize in the form of liquid crystalline masses within the paint layers. When they expand beyond the paint layer, they distort the paint and may erupt at the surface where they protrude or even extrude. These deformations are now recognized in thousands of paintings. Many of these metal soap masses furthermore mineralize forming minium (lead plumbate) and/or leadhydroxy/chloride-carbonates in lead soap or zinc carbonates in the case of zinc soaps. Generally the volume changes due these processes are minimal although the metal soap may grow into larger masses of 100-200 micron diameter. This theory could be developed by an integrated molecular level approach involving GCMS and DTMS work and various forms of chemical microscopy using SIMS, FTIR, Raman and SEM-EDX. The paper furthermore shortly summarises the outcome of the so-called *MOLART* approach applied to many different problems in paintings in the period 1995-2006.

¹ Molecular Paintings Research Group, AMOLF, Amsterdam, NL

Introduction

When a painting becomes a finished picture it has to dry physically by evaporation of water or solvent, and chemically by reaction of air with the binding medium constituents to form a non-sticky viscous mass that keeps the pigment particles in place. So when the painter is satisfied with the picture, a lot of processes are starting up to solidify the painted creation. These same processes however are also responsible for undesirable changes that take place later on when the work ages. Changes that will require the attention of conservators in charge of maintaining the quality of the visible surface and the structural integrity of the paint layers and support. Research on the nature of these materials in paintings and their compositional changes with time i.e. the molecular aspects of ageing was at the centre of the attention of the MOLART programme supported by NWO and its sequel the De Mayerne Programme. Both research programmes were multidisciplinary in nature and were successful because of the close collaboration of art technical historians, conservators and art scientists interested in material science aspects of works of art.

The MOLART approach

Addressing molecular aspects requires a more molecular level approach to the nature of the materials used in paintings and after several centuries a determination of the present condition of these materials. It was our view that the painting itself was the best source of information on its making, condition and composition and it was our challenging task to extract that information with minimal intervention. For that purpose we used mass spectrometry as the technique to obtain molecular level information on the organic substances in paintings and various spectroscopic methods to get information about the inorganic substances. Direct temperature resolved mass spectrometry (DTMS) proved very useful for characterisation of varnishes, resins, waxes, conservation materials and the organic constituents in minuscule paint particles selected under the microscope. Complementary GC/MS, Pyrolysis GC/MS and HPLC/MS were used for identification of compounds purified by chromatography (see for example Van den Berg et al. 1998; Van der Doelen 1999; Scalerone et al. 2003; Van den Berg 2002; Theodorakopoulos 2005). As a beta-site for the Stingray Reflection Imaging FTIR microscope in 1998 we were the first to explore the potential of this technique for paintings studies and showed that lead soaps - now recognized as a potential problem in many paintings - are easily detected with this technique (Heeren et al. 1999; Van der Weerd et al. 2002; Vaqn der Weerd 2002b). Spot analysis using laser desorption ionisation mass spectrometry proved suitable for identification of synthetic dyes and pigments (Wyplosz 2003), but lacked the resolution required for paint cross section studies. Experiments with microscopy mass spectrometry in our laboratory at the end of the 20th C already showed the great potential of secondary ion mass spectrometry as a technique to obtain information on the distribution of organic as well as inorganic constituents of paint (Keune and Boon 2004). The PhD thesis work of Keune (2005) and Marino (2006) present various studies of traditional oil paintings from the 16th to 20th C using imaging SIMS as main analytical technique. Best results are obtained when different imaging data sets from FTIR,

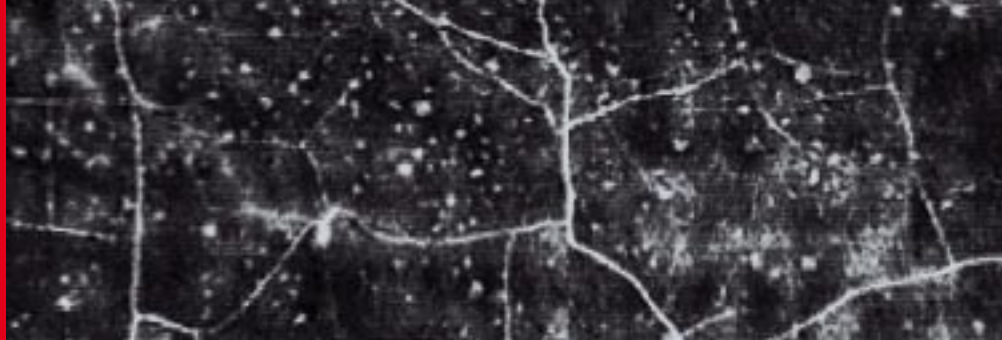


Fig. 1. Lead soaps are visible as white dots in a positive print of the X-ray of *The Anatomy Lesson of Dr. Nicolaes Tulp* painted by Rembrandt van Rijn in 1634 (MH 146). Average diameter of the dots is about 100 micrometer. Note the craquelure for the size. The original picture has been processed in Photoshop CS2 to illustrate the phenomenon.

SEMEDX, SIMS and LM are combined by careful overlaying to relate the information to the layer structure and distribution of constituents within the layers. This MOLMAP approach has led to new insight into the discoloration of smalt (Boon et al. 2001), blackening of vermilion (Keune and Boon 2005), whitening of bone black (Van Loon et al. 2005), destabilisation of CdS pigments (Burnstock et al. 2005), dissociation of lead tin yellow I pigments (Boon et al. 2004) and the reactivity of lead white leading to lead soap aggregates, pitting and paint loss, efflorescent crusts, changes in hiding power and transparency (Boon et al. 2002; Noble et al. 2005; Keune and Boon 2007). These studies have benefited tremendously from close collaboration with conservators in museums locally and worldwide or with those colleagues working in our laboratory on the paintings ensemble of the Oranjezaal (Van Loon et al. 2006).

The Oranjezaal project directed by Van Grevenstein (this volume) provided the unique opportunity to study the condition of paintings in an environment that has remained virtually undisturbed since 1650. The AMOLF team certainly became fascinated by the many unexpected changes that had taken place in the paints. Two other forms of collaboration and information exchange facilitated by the NWO programmes should be mentioned. The Open Laboratory agreement of AMOLF with the Royal Cabinet of Paintings The Mauritshuis in the Hague invited conservators into our AMOLF laboratory and also provided opportunities for our chemists to work closely on relevant questions concerning the chemical changes in and below the surface of paintings by Rembrandt, Vermeer, Van der Neer, Hals and others. Our 6-weekly Pigment and Paint Working Group meetings at AMOLF were an open forum for conservators to directly respond to and interact with the latest findings by our PhD students while given opportunities to pose and present challenging research questions. These forms of intellectual interactions educated us and acted as an important vehicle for knowledge transfer and new approaches.

Reactivity of oil binding medium components

The awareness of the wide spread global occurrence of metal soap aggregates in paintings has developed in less than a decade. The restoration of *The Anatomy Lesson of Dr. Nicolaes Tulp* by R. van Rijn (pixit 1634; MH 146) was the start of a thorough investigation of the painting technique and its present condition. The abundance of peculiar pustules was particularly striking. These had been reported before but they were attributed to fire damage that the painting endured in 1723 (De Vries et al 1978). Investigation by imaging FTIR and SIMS microscopy demonstrated that these organic aggregates were composed of lead soaps. The lead soap aggregates were present in large numbers as could be deduced from X-ray pictures examined

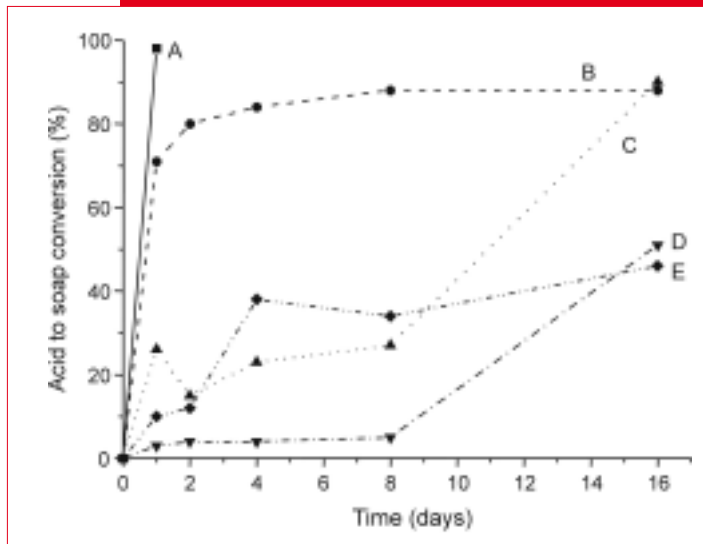


Fig. 2. Lead soap can form at ambient temperature by reaction of lead compounds and palmitic acid. Lead soap formation was monitored by FTIR. Lead soap (%) = $100\% * I(1510) / [I(1510) + I(1705)]$

under the stereomicroscope (Fig. 1). These aggregates turned out to be present in many more paintings in the Mauritshuis and are now recognised in other collections as well. A recent survey of the Tudor-Stuart collection of Tate Britain shows lead soap aggregates in more than 60% of the paintings (Jones et al. 2007).

The occurrence of lead soap aggregates points to an oil paint defect. The MOLART working model on aging of oil paint (Boon et al. 1997) proposed a transition from a cross linked plant oil to a metal coordinated paint system, because a rather extensive hydrolysis had been observed of the biological ester bonds in the cross linked polyunsaturated triglycerides. Investigations by Van den Berg et al. (1999) on oil paint models and samples from paintings and recent studies on alkyd oil paints (Schilling et al. 2007) demonstrate the extensive hydrolysis that takes place in a time frame of 50-100 years. The process of degrouping of the cross linked oil components into their biochemical components of glycerol, fatty acids, diacids and some cross linked polyacid moieties should lead to a complete failure of the paint and loss of the picture. That this usually does not happen is caused by a self-repair mechanism in which lead binds these loose ends with limited volume change into a metal coordinated network. The hypothesis that the acids rapidly react with available metals present as driers or metal containing pigments like lead white was supported by experiments with palmitic acid that reacts freely at room temperature with lead white and can dissolve it completely while forming lead soaps (Hoogland and Boon 2005). Fig 2 shows lead soap formation as a function of temperature for several lead compounds with palmitic acid. Lead acetate reacts most rapidly while lead tin yellow takes a little bit longer but most of the mineral matter has reacted away within half a month. Four-year-old lead white paint reconstructions made by L. Carlyle for MOLART in 1999 formed lead soaps under high relative humidity (80% RH) and at higher temperature (50 °C) in a matter of one month of exposure. The SIMS data of the surface of these reconstructions in Fig 3 demonstrates the increase in lead soap mass peaks of the palmitic and stearic acid while FTIR confirms an increase in the metal carboxylate absorption at 1520 cm^{-1} (FTIR data not shown). It is our idea that azelaic acids will form a relatively stable metal coordinated network because of their chain

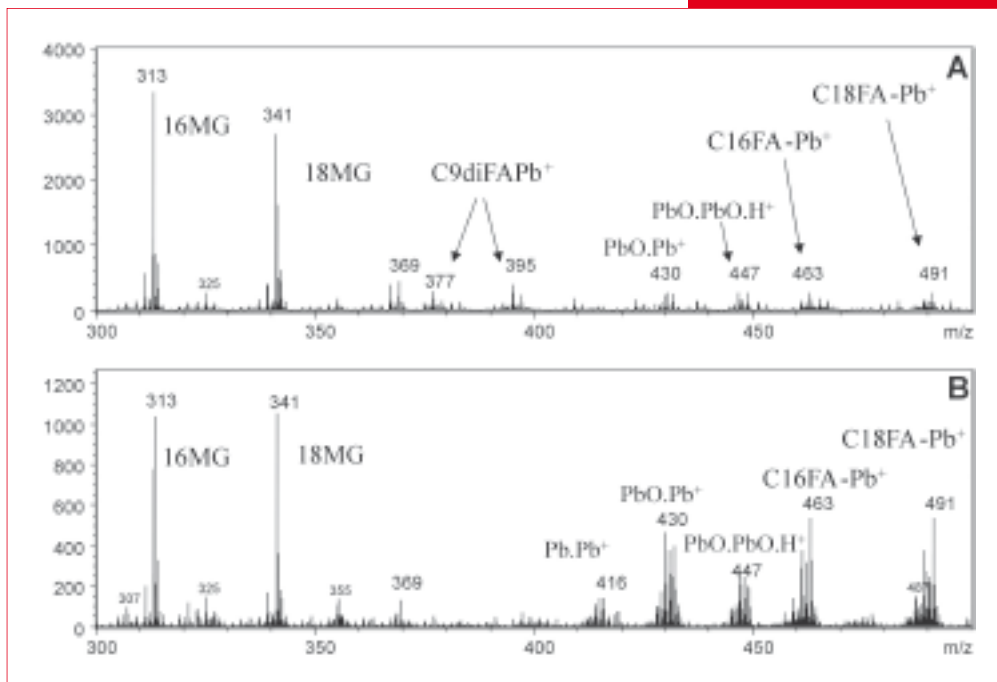


Fig. 3. Secondary Ion Mass Spectra of lead white paints (coded ZD prepared and aged by Carlyle) before and after a 30 day exposure to high relative humidity (80%) at elevated temperature (50 °C). See also Keune (2005).

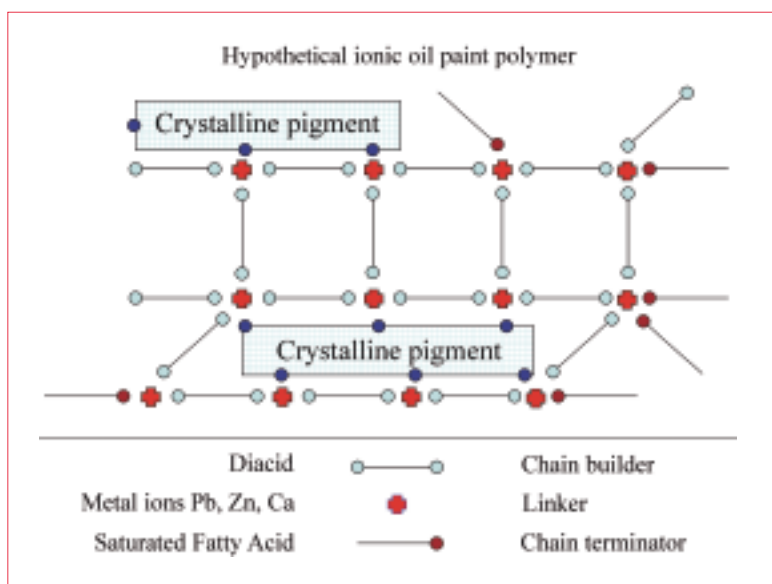


Fig. 4. Proposed structure of metal coordinated oil paint, in which diacids form a 3D structure when coordinated by lead. Monocarboxylic acids are chain terminators that limit the size of the ionomeric polymer.

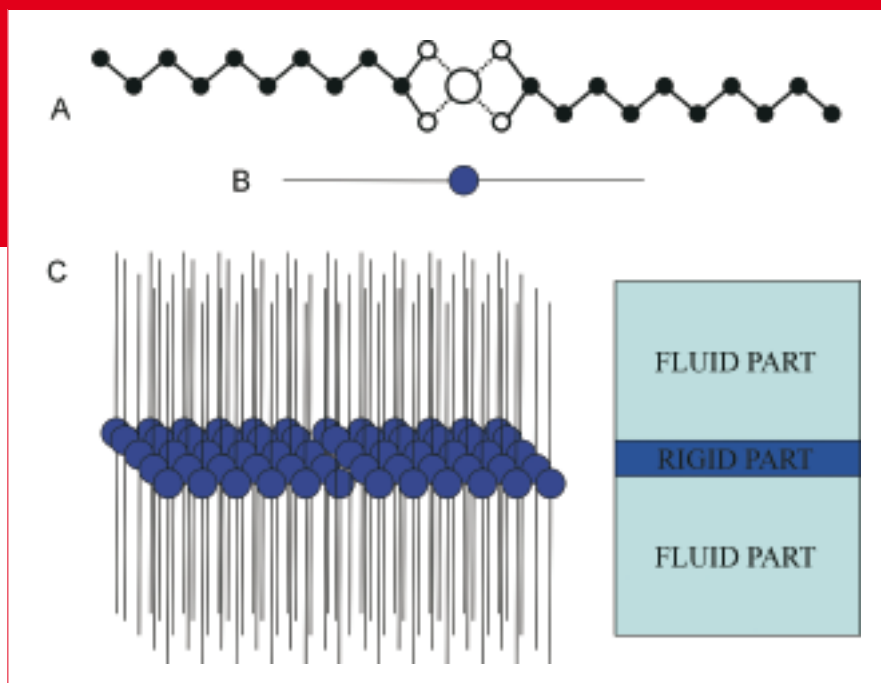


Fig. 5. Lead soaps form liquid crystals in which the metal coordinated carboxylic acids form raft-like structures with fatty acyl chains perpendicular to these rafts. This splayed chain structure has been proposed by Corkery (1997).

building ability in 3D while monocarboxylic acids can only act as chain terminating units. This process appears to start already during the cross-linking and oxidation stage of the drying of oilpaint as deduced from solid state NMR data (Verhoeven et al., this volume). A possible model structure is shown in Fig. 4 where the diacids as dumbbells coordinated by lead (red crosses) link the various lead white crystals in a metal coordinated 3D network. If such a structure is compromised by acid from environmental sources or by anions that compete with the relatively weak fatty acid carboxyl groups, the coordination of the diacid structure could be locally lost temporarily, while monocarboxylic acids may lose their connection with such a network permanently and migrate to form separate apolar lead soap masses. FTIR, Raman and XRD studies of synthetic lead soaps of longer chain fatty acids demonstrate that lead soaps organise themselves preferentially in liquid crystals¹ as splayed chain systems (Corkery et al. 1997). The metal carboxylates can form relatively stable rafts with long chain fatty acids closely packed by Van der Waals forces projecting above and below a metal carboxylate plane (Fig. 5). At higher temperature these fatty acyl chains transform into relatively disorganised almost liquid like cushions. This flexibility of metal soap rafts provides a lot of potential for movement in and between paint layers and might explain the appearance of lead soaps at the

¹ The idea of metal soap liquid crystals as possible components of paints was first introduced by Corkery during the Metal Soap meeting in the Van Gogh Museum on 10 september 2005.

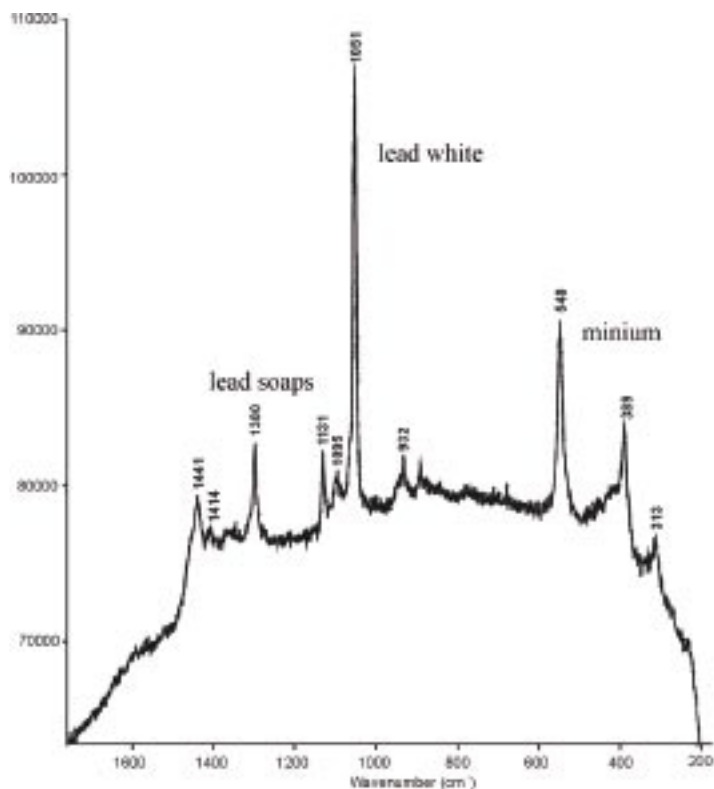
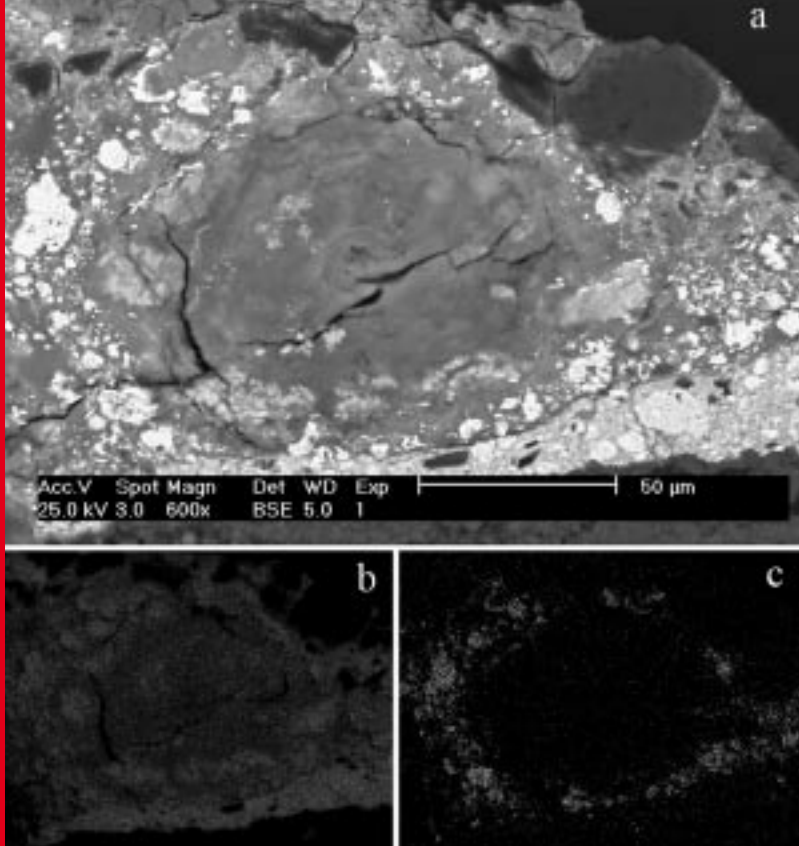


Fig. 6. Raman spectrum of mineralised lead soap aggregate from a paint cross section of the Herald by Christiaan van Couwenbergh (Oranjezaal HTBS43) in which larger newly formed orange minium crystals, lead white nanocrystals and lead soaps co-occur in a lead white ground (arrow points to the analysed spot). The size of the aggregate is about 120 micrometer. See also Keune 2005. The Raman data were obtained at the Metropolitan Museum Scientific Department in New York with kind assistance of Sylvia Centeno.

surface of paintings. The key to understanding the lead soap formation in paintings are reactive monocarboxylic acids. Here we should recall that paintings are multilayer systems where some paint layers may be medium rich but “underbound” with respect to coordinating metals, while others are lead (white) rich and presumably medium poorer. Lead poor paint layers are a potential source of mobile reactive fatty acids. Fatty lead white grounds are potentially an important source of lead soaps. Since we have so few data on the quantitative aspects of the distribution of mono and dicarboxylic fatty acids in paint layers, we propose that the stoichiometry of lead and fatty acids in paint layers with and without lead soap aggregates should be studied in detail to understand the various quantitative aspects of the phenomenon.

Lead is not the only metal of importance. Apart from lead, metals like copper, zinc, iron, aluminum, earth alkali elements like calcium and alkali elements like potassium can form carboxylates, which we may encounter in paint layers. Potassium leaches from smalt (cobalt potash glass) and potassium soaps have indeed been demonstrated recently (Spring et al. 2006). Calcium soaps are very versatile and may play a major role in the stabilisation of paints but their presence remains to be demonstrated. Aluminum soaps are common additions to modern oil paints but a disadvantage is their hydroscopicity leading to hydroxy-derivatives (Corkery 1998). The saturated fatty acids in aluminum stearates do not contribute to the paint structure after hydrolysis. In fact residual hydroxy-aluminum soaps can form micelles that may be responsible for the recently observed water solubility of about 40-50 year old oil paints (Burnstock et al. 2007).

Fig. 7. SEM Electron Back Scatter picture (BSE) (a) and the element maps of lead (b: PbM line) and tin (c: Sn L line) in a cross section of a lead tin yellow paint (LTY I) from the Sherborne Retable (Sherborne Abbey Almshouse, Dorset). Residual lead stannates are accumulated around the growing lead soap mass. Inside the lead soap mass new mineralization of lead white is visible with a medium BSE reflectivity. Most of the lead occurs in a finely divided form inside the lead soap structure. See also Boon et al. (2004) and Keune (2005).



Mineralisation of lead soap structures

Metal soap aggregates undergo a process of mineralisation, which might be beneficial because it can stabilise them. Minium (leadplumbate) has been identified in some aggregates (Boon et al. 2002; Van der Weerd et al. 2002) and this mineral appears to form, in my opinion, when the aggregates are protected from a direct contact with the atmosphere. Many protruding aggregates that we observed contain lead carbonates which appear to be in the form of hydrocerussite (leadhydroxycarbonate) but the aggregates are often remarkably rich in chlorides so the presence of phosgenite (leadchlorocarbonate) must be considered. Phosgenite can epitaxially grow on cerrusite demonstrating their structural compatibility (Pina et al. 1996), and a similar compatibility is expected for leadwhite. The chlorides are most easily detected with SIMS in the negative ion mode but the nanocrystals still remain to be crystallographically characterised. The Raman spectral spot analysis of a partially mineralised aggregate in a lead white oil ground in the *Herald* in the Oranjezaal ensemble in Fig 6 demonstrates minium, lead white (plus phosgenite?) and lead soap posing new questions about the chemical conditions of their formation. Mineralising zinc soaps in paints on a Van Gogh painting *Falling leaves; Les Alyscamps* were found to contain zinc carbonate (Keune 2005). Lead soap masses can be so forceful in their crystal growth that they separate lead tin yellow I pigments into fragments that are oriented around the lead soap mass (Boon et al. 2004). Further remineralisation leads to very complex SEM-BSE pictures of such paints where the submicron crystals of the

new minerals can be discriminated from the coarser leadstannate residues (highest BSE signal) of the original degraded pigment that have accumulated around the lead soap aggregates (Boon et al. 2004). Fig. 7 demonstrates this in a paint cross section from a 15th C triptych painting (Sherborne retable) possibly made by the Master of Alkmaar, in which the tin (Sn in Fig c) marks the distribution of the residual leached lead tin yellow particles while the lead (Pb in Fig b) is present all over in dispersed and more mineralised forms.

Mineralisation also occurs on the surface of the paint or even on top of the varnish when an efflorescing crust of lead soaps reacts with atmospheric gases obscuring the picture. SIMS studies of efflorescent crusts on a canvas from the estate of F.E.Church (Olana) shows the presence of free fatty acids, fatty acyl monoglycerides and lead soaps (Van den Berg 2002; Van der Weerd 2002). Efflorescent crusts on bone black paint on a 16th C ceiling in the Johan de Witt house in the Hague (Van Loon et al. 2005) are complex white crusts that consist of lead soaps mineralised with lead white, phosgenite and anglesite crystals. Similar crusts have been identified recently on a 19th C paintings by Bosch-Reitz (Keune et al. 2007). We postulate that many efflorescent crusts on paints are mineralised by reaction of lead soaps with atmospheric gasses.

Physical effects

Lead soap formation inside paintings or near the surface has consequences for the stability of the paint layers and the light reflection. Lead soap aggregation deforms the paint layers while protruding lead soap masses lead to a grainy sandy texture, paint loss, pitting and accumulation of dirt in local spots (Noble et al. 2002).

Dissolution of lead white leads to increased transparency of the paints and loss of reflected light, which may make the color darker. In the case of pigment mixtures, the color balance can be lost. Lead tin yellow paints are known to form an orange peel texture due to lead soap protrusions but the color change is another aspect that is due to a loss of lead oxides from the pigment and the appearance of lead soaps that partially mineralise into a semi transparent white. As a consequence lead tin yellows are lighter yellow than intended originally. The mobility of fatty acids and metal soaps is largely a physical process that is driven by gradients in temperature and moisture. Since these are slow processes, they easily span the professional life of a conservator. Documentation of paint layers preferably by X-ray nanotomography would be a desirable way to monitor paintings, but we have to inventory on a much grander scale how many paintings are affected and why certain paintings do not show lead soap mobility at all.

Concluding remarks

Painters could not anticipate how much their paintings would change because of intrinsic factors such as the paints, their working methods, the instability of the oil paint system and external factors like moisture, variable temperature, light conditions and noxious gasses. Self-repair mechanisms in paintings discovered in the course of the two programmes rescue the painting but do affect the picture. We still

understand very little of the many slow processes that take place in paintings and how they change the pictures. The support of the MOLART and De Mayerne programme has enabled us to study these processes in a qualitative manner and has made it possible to estimate the magnitude of the occurrence of metal soap related defects in collections world wide. This is the tip of the iceberg. The main concern now is to find out how environmental conditions and conservation practices may accelerate or decelerate these processes that so deeply affect the quality of the picture and the properties of all the paint layers. This is a gigantic task that will need the combined efforts of conservators and art scientists in conservation research programmes and requires the support of the professional organisations like ICOMCC, IIC, AIC and money from national and international funding agencies.

Acknowledgements

The De Mayerne programme part carried out at AMOLF owes much to the creative and scientific input from the PhD student group (I. Pastorova, G. van der Doelen, O. van den Brink, J. van den Berg, J. van der Weerd, N.Wyploszcz, G. Languri) during the MOLART period, and K. Keune, A. van Loon, B. Marino, F. Hoogland during the De Mayerne period. I am thankful to R.M.A. Heeren, K.J. van den Berg, R. Hoppenbrouwers for their efforts and assistance in setting up the MOLART approach. I am indebted to Alan Phenix, Leslie Carlyle, Aviva Burnstock, Petria Noble, Anne van Grevenstein, Ester Ferreira, Lidwien Speleers and J.R.J. van Asperen de Boer for their collaborative input and efforts to keep the research relevant for art science and the conservation field. We gratefully acknowledge the participation of many museums and the Oranjezaal research consortium that provided so many samples for our studies. Much is owed to the participants - especially Patricia Noble - in the Open Laboratory agreement between AMOLF and the Mauritshuis. The research was supported by FOM via the approved programmes 28 and 49 and by NWO via support to the De Mayerne project MOLMAP and MOLART Priority Programme.

References

- Boon J.J., Peulvé S., Van den Brink O.F., Duursma M.C., Rainford D. (1997). Molecular aspects of mobile and stationary phases in ageing tempera and oil paint films. In: *Early Italian Paintings: Techniques and Analysis* (T. Bakkenist, R. Hoppenbrouwers and H. Dubois eds). Limburg Conservation Institute (SRAL), Maastricht, p. 35-56
- Boon J.J., Keune K., Van der Weerd J., Geldof M., Van Asperen de Boer J.R.J. (2001). Imaging microspectroscopic, secondary ion mass spectrometric and electron microscopic studies on discoloured and partially discoloured smalt in crosssections of 16th century paintings. *Chimia*, 55, p. 952-960.
- Boon J.J., Van der Weerd J., Keune K., Noble P., Wadum J. (2002). Mechanical and chemical changes in Old Master paintings: dissolution, metal soap formation and remineralization processes in lead pigmented ground/intermediate paint layers of 17th century painting. In: *13th Triennial Meeting of the ICOM Committee for Conservation in Rio De Janeiro Preprints* (R. Vontobel ed), James & James, London. p. 401-406.
- Boon J.J., Gore E., Keune K., Burnstock A. (2005). Image analytical studies of lead soap aggregates and their relationship to lead and tin in 15th C lead tin yellow paints from the Sherborne triptych. In: *IRUG6 Conference 2004 Florence* (M. Picollo, ed), Il Prato, Padova, p. 66-74
- Leone B., Burnstock A., Jones C., Hallebeek P., Boon J.J., Keune, K. (2005). Deterioration of Cadmium Sulphide Yellow Artists' Pigments. In: *Proceedings of the 14th Triennial Meeting of the ICOM Committee for Conservation in The Hague* (I. Verger ed), James & James, London, Preprints 2, p 803-813
- Burnstock A., Van den Berg K.J., De Groot S., Wijnberg L. (2007). An investigation of water sensitive oil paints in 20th century paintings. In: *Modern Paints Uncovered* (T.S. Learner, P. Smithen, J. Krueger and M.Schilling), Proceedings from the Symposium in London. Getty Publications, Los Angeles. In press.
- Corkery R.W. (1997). Langmuir-Blodgett (L-B) multilayer films. *Langmuir, The ACS journal of surfaces and colloids*. 13, p.3591-3595.
- Corkery, R.W. (1998). Artificial biomineralisation and metallic soaps. PhD dissertation Australian National University, Canberra.
- De Vries A.B., Tóth-Ubbens M., Froentjes W. (1978), Rembrandt in het Mauritshuis, Alphen aan de Rijn, p. 89.
- Heeren R.M.A., Boon J.J., Noble P., Wadum J. (1999). Integrating imaging FTIR and secondary ion mass spectrometry for the analysis of embedded paint cross-sections. In: *Proceedings of the 12th ICOM-CC Triennial Meeting in Lyon*, (J. Bridgland ed) James and James, London. p. 228-233
- Hoogland F., Boon J. J. (2005). Unpublished. Reported at the ICOMCC Scientific Research Working Group interim meeting on lead soaps in collaboration with MaSC held in the Van Gogh museum in Amsterdam on 10 september 2005.
- Jones R., Townsend J.H., Stonor K., Duff N. (2007). Lead soap aggregates in sixteenth and seventeenth century British paintings. In: *AIC Paintings Working Group Meeting 2006 Postprints* (Helen Parker ed). In press.
- Keune K., Boon J. J. (2004). Imaging secondary ion mass spectrometry of a paint cross-section taken from an early Netherlandish painting by Rogier van der Weyden. *Analytical Chemistry*, 76 (5): p. 1374-1385.
- K, Boon J. J. (2005). Analytical imaging studies clarifying the process of the darkening of vermilion in paintings, *Analytical Chemistry*, p. 4742-4750.
- Keune K. (2005). Binding medium, pigments and metal soaps characterised and localised in paint cross-sections. PhD Thesis University of Amsterdam. pp. 181. Report of MOLART Series: MOLART11, AMOLF, Amsterdam.
- Keune K., Kirsch K., Boon J.J. (2007) Lead soap efflorescence in a 19th C painting: appearance, nature and sources of materials. In: *AIC Paintings Working Group Meeting 2006 Postprints* (Helen Parker ed). In press.
- Keune K. and Boon J.J. (2007) Insights into the lead soap aggregate formation in oil paintings with analytical imaging studies. *Studies in Conservation*, in press
- Marino, B. (2006) Paints quantified: Image analytical studies of preparatory grounds used by Van Gogh PhD thesis University of Amsterdam. Report of MOLART Series: MOLART 12, AMOLF, Amsterdam.

- Noble P., Boon J.J., Wadum J. (2002). *Dissolution, Aggregation and Protrusion: Lead soap formation in 17th century grounds and paint layers*. *ArtMatters* 1, p. 46-62.
- Noble P., Van Loon A., Boon J.J. (2005). *Chemical changes in old master paintings II: darkening due to increased transparency as a result of metal soap formation processes*. In: *Conference Proceedings 14th Triennial Meeting of the ICOM Committee for Conservation in The Hague* (I. Verger ed.), James & James, London, p 496-503
- Pina C.M., Fernandez-Díaz L., Prieto M. (1996). *Topotaxy relationships in the transformation phosgenite-cerrusite*. *J Crystal Growth* 158, 340-345.
- Scalarone D., Van der Horst J., Boon J.J., Chiantore O. (2003). *Direct-temperature mass spectrometric detection of volatile terpenoids and natural terpenoid polymers in fresh and artificially aged resins*. *Journal of Mass Spectrometry*, 38: p. 607-617
- Schilling M.R., Mazurek J., Learner T.S. (2007). *Studies of Modern Oil-Based Artists' Paint Media by Gas Chromatography/Mass Spectrometry*. In: *Modern Paints Uncovered* (T.S. Learner, P. Smithen, J. Krueger and M. Schilling), *Proceedings from the Symposium in London*. Getty Publications, Los Angeles. In press.
- Spring M., Higgitt C., Saunders D. (2005). *Investigation of Pigment-Medium Interaction Processes in Oil Paint containing Degraded Smalt*. *National Gallery Technical Bulletin* 26, 56-69.
- Theodorakopoulos C. (2005). *The excimer laser ablation of picture varnishes. An evaluation with reference to light-induced deterioration*. PhD thesis Royal College of Art, London, UK.
- Van den Berg J.D.J., Boon J.J., Van den Berg K.J. (1998). *Identification of an original non-terpenoid varnish from the early 20th century oil painting „The White Horse“ (1929) by H. Menzel*. *Analytical Chemistry*, 70, p. 1823-1830.
- Van den Berg J.D.J., Van den Berg K.J., Boon J.J. (1999). *Chemical changes in curing and ageing oil paints*. In: *Proceedings of 12th Triennial ICOM-CC Meeting Lyon*, (J. Bridgeland ed), James and James, London. p. 248-253
- Van den Berg J.D.J. (2002). *Analytical chemical studies on traditional linseed oil paints*. PhD thesis University of Amsterdam. Report of MOLART Series: MOLART 6, AMOLF, Amsterdam.
- Van der Doelen G.A. (1999). *Molecular studies of fresh and aged triterpenoid varnishes*. PhD thesis University of Amsterdam. Report of MOLART Series: MOLART 1, AMOLF, Amsterdam.
- Van Grevenstein-Kruse, A. (2006). *Multidisciplinary research on the paintings ensemble in the Oranjezaal of the Royal Palace Huis ten Bosch*. In: *Reporting Highlights of the De Mayerne Programme* (J.J.Boon and E. Ferreira eds). This volume, p. 97-108.
- Van Loon A., Boon J.J. (2005). *The whitening of oil paints films containing bone black*. In: *Conference Proceedings 14th Triennial Meeting of the ICOM Committee for Conservation in The Hague* (I. Verger ed.), James & James, London, p. 511-518
- Van Loon A., Speleers L., Ferreira E.S.B., Keune K., Boon J. J. (2006). *The relationship between the degree of preservation and painting technique in the Oranjezaal ensemble, Huis ten Bosch palace*. In: *The Object in Context: Crossing Conservation Boundaries* (D. Saunders et al eds), IIC, London, p. 218-223
- Van der Weerd J., Boon J.J., Geldof M., Heeren R.M.A., Noble P. (2002). *Chemical changes in old master paintings: dissolution, metal soap formation and remineralization processes in lead pigmented paint layers of 17th century paintings*. *Zeitschrift für Kunsttechnologie und Konservierung*, 16, p. 36 - 51.
- Van der Weerd J. (2002b). *Microspectroscopic Analysis of Traditional Oil Paint*. PhD thesis University of Amsterdam, Report of MOLART Series: MOLART 7, AMOLF, Amsterdam.
- Verhoeven M.A., Carlyle L., Reedijk J. and Haasnoot J.G (2006). *Exploring the application of solid-state Nuclear Magnetic Resonance to the study of the deterioration of paintings*. In: *Reporting Highlights of the De Mayerne Programme* (J.J.Boon and E. Ferreira eds). This volume, p. 33-42.
- Wyplosz, N. (20003). *Laser desorption mass spectrometric studies of artists' organic pigments*. PhD thesis University of Amsterdam, Report of MOLART Series: MOLART 8, AMOLF, Amsterdam.

Exploring the application of *solid-state* Nuclear Magnetic Resonance to the study of the deterioration of paintings

COORDINATION CHEMISTRY OF LEAD CARBOXYLATES IN OIL PAINTINGS

Abstract:

In this contribution the use of *solid-state* Nuclear Magnetic Resonance (NMR) for the study of the ageing process in oil paintings is explored. *Solid-state* NMR is an excellent technique to study the chemical properties of amorphous solid material. From a chemical point of view the issues of ageing and deterioration of oil paintings are concentrated around the interaction between inorganic pigments and organic binding medium. In this case, the reactivity of (basic) lead carbonates, occurring in white lead pigment and the chemically cross-linked triglyceride network were of interest. Both ¹³C and ²⁰⁷Pb NMR were applied to study some relevant paint samples and their components. The main constituents of a typical lead white oil paint found in old paintings were studied separately, e.g. the cured paint network, lead pigments and previously described deterioration products, followed by historically accurate paint reconstructions. The main observation regarding ageing of paint is that the chemical reactions between lead pigments and the available free acids groups of the binding medium is largely complete within 5 years after paint application.

¹ Coordination and Bioinorganic Chemistry, Leiden Institute of Chemistry, P.O. Box 9502, 2300 RA Leiden, The Netherlands

² Tate Britain, Millbank, London, SW1P 4RG, England, leslie.carlyle@tate.org.uk

Introduction

General Introduction

The formation of lead aggregates (lead carboxylate) in paint layers, which protrude into the surface of oil painting disrupting the image is a serious problem for historical oil paintings (16th to 19th century). Curators in museums are encountering this defect in a growing number of paintings, some Masterpieces included. It is now generally accepted that protrusions into the surfaces of these paintings are the consequence of chemical alterations that occur in the paint film over time. In many cases protrusions are observed in paint layers that contain lead white, lead oxides or lead tin yellow (Boon et al. 2002; Noble et al. 2002; Higgitt et al. 2003; Boon et al. 2005; Keune 2005; Noble et al. 2005). Since lead compounds are ubiquitously present in traditional oil paints, it is of utmost importance to understand their role in the formation this defect. As determined with analytical chemical techniques, like GC-MS, SIMS and IR-imaging the protrusions contain high concentrations of lead carboxylates with long saturated alkyl chains *i.e.* lead stearate and palmitate (van der Weerd et al. 2001; Higgitt et al. 2003; Keune 2005). The literature on modern paint describes chemical reactions that may be relevant for the appearance of the chemical compounds detected during deterioration of paint film (Muizebelt et al. 1998; Mallegol et al. 1999; Mallegol et al. 2000; Muizebelt et al. 2000). For instance, oxidation of the (per)oxy cross links, that arise during the chemical 'drying' of the paint, lead to breakage in the oxidatively cross-linked part of the initial network under the formation of free acid groups. In addition, early GCMS studies on paints have shown that hydrolysis of ester bond in the cross linked binding medium of oil paints in paintings is a widespread phenomenon that is presumably a consequence of exposure to environmental moisture, (Boon et al. 1997; Van den Berg et al. 2001). These studies showed that in the first hundred years after paint application approximately 90% of the potentially available acids groups are liberated. A new model for oil paint was proposed that involved metals ions such as Pb^{2+} as coordinating constituents to account for the present-day stability of the paint layers. It can be anticipated that the oxidation and saponification processes described above lead to the partial transformation of the binding medium from a cross linked triglyceride network to free fatty (di)acids (Plater et al. 2003) while co-ordination of metal atoms from the pigments to these acids leads to a network of ionomers comprised of metal ions, diacids and non-reactive carboxylates. After these chemical transformations the incompatibility of the different components could lead to the separation of the stearate/palmitate fraction from the bulk with as a possible consequence the accumulation of lead carboxylate aggregates. From a chemical point of view it is important to understand why and how the processes described above are taking place. For instance, the chemical reactivity of the binding medium alone is understood reasonably well, while its behaviour in paint in the presence of pigments over the longer period of time is less straightforward. Of interest as well is the thermodynamic stability of the system of components that arise over time and the mechanism and driving force behind aggregation that lead to protrusions.

To obtain knowledge on the intricate system of pigment and oil degradation products, it is important to first have a firm knowledge of the separate building

blocks. At the same time it is important to develop a model system that closely resembles historical paint. This model system can then be chemically manipulated to obtain access to its chemical properties. In this way the results can be extrapolated to historic paintings. The objective of our study is to report the insight gained in the co-ordination chemistry of the lead carboxylates and carbonates in the processes that are taking place in ageing oil paint networks. Our approach is to monitor the co-ordination of lead ions that is taking place in the paint by ^{13}C and ^{207}Pb *solid-state* Nuclear Magnetic Resonance (NMR) techniques.

Solid-state Nuclear Magnetic Resonance

NMR spectroscopy is applied by putting a sample in a strong magnetic field while observing the response or 'resonances' of the atoms of relevant molecules in the sample. The benefit of *solid-state* NMR is that the atoms that are sensitive to the magnetic field can be observed directly inside the paint layer. In this sense the technique is non-invasive. It can be applied to amorphous solids and is not dependent on higher level ordering like crystal packing. Commonly observed are the nuclei of nitrogen (^{15}N) and carbon (^{13}C) atoms but also a number of metals can be used for instance lead (^{207}Pb), which is explored in this study. Compared to other analytical methods NMR is considered intrinsically insensitive, implying that a sample volume of at least 20 mm^3 is required to obtain sufficient signal-to-noise in a reasonable time. The suitability of a nucleus depends on its natural abundance and susceptibility to the magnetic field. For instance carbon-13 occurs in 1.1% compared to 98.8% for the NMR silent carbon-12 (^{12}C). The susceptibility of the NMR sensitive lead-207 nucleus (^{207}Pb) is ~ 0.83 of carbon-13 while its natural abundance is 22.1%, resulting in a relative more sensitive nucleus (Parella 1998). The position of the signal of an atom in the NMR spectrum is called the 'chemical shift' and depends primarily on the chemical functionality of an atom in a molecule. Not only the difference between functional groups e.g. acid, ether or methyl can be distinguished but also the difference between the carbonyl groups of an ester, acid, its conjugated base or a metal carboxylate, which are relevant to our studies. In conclusion, the strength of NMR in the context of this research is the qualitative analysis of the chemical composition of samples with several components in a non-invasive way.

Materials and Methods

Preparation of lead salts

The preparation of lead carboxylates has been described before (Tarbutton and Vosburgh 1932; Plater et al. 2003). The model of the ionomeric network was synthesised by autoxidation of ethyl linoleate (Warzeska et al. 2002) after 2 weeks followed by hydrolysis of the esters and subsequent reaction with a lead source as above.

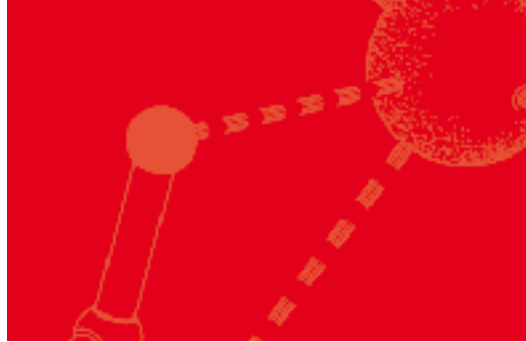
Historically accurate reconstructions

Reconstructions have been prepared before, the sample coding is as follows: Z freshly pressed linseed oil, D Dutch process Lead White and AC treated with lead acetate as drier, the ratio of pigment to drier was ~ 3 (Carlyle 2000). For NMR experiments the

material was carefully removed from its Mylar support and divided in small pieces to fit in the NMR rotor. For comparison some fresh samples were prepared according to the same methods.

Solid-state NMR experiments

All spectra have been recorded on a Bruker DMX-400 9.4 T spectrometer equipped with a 4 mm MAS probe. *Carbon-13 NMR*: Spectra have been recorded with a standard cross-polarisation experiment (Metz et al. 1994). TPPM proton decoupling was used with a power of ~50 kHz (Bennet et al. 1995). Glycine was used as a secondary reference for ^{13}C relative to tetramethylsilane. *Lead-207 NMR*: Spectra have been recorded with a rotor-synchronised Hahn-echo experiment to prevent probe ringing. TPPM decoupling was applied during echo and acquisition at ~35 kHz. The ^{207}Pb pulse powers were set to ~80 kHz to achieve a broad irradiation. The initial excitation was accomplished by a $\pi/2$ pulse. The lead spectra were recorded at 303 K to assure identical experimental condition for the temperature-sensitive chemical shift of the ^{207}Pb nucleus. Spectra were recorded at 300 or 500 kHz spectral widths and for each spectrum the transmitter frequency was tuned to the approximate middle of the initial signal. To identify the isotropic chemical shift value the rotor was spun at 11 and 12 kHz. A saturated lead nitrate solution was used as a secondary reference at -2970 ppm with respect to tetramethyllead (Fayon et al. 1997).



Results and Discussion

Comparison of the ^{13}C NMR spectra of lead salts

Figure 1 represents the carbon spectra of an oil paint layer and three of the compounds that can be encountered in a paint layer and that are relevant to the subject of ageing and deterioration. The paint sample (Figure 1a) shows resonances between 0-50 ppm that can be attributed to the methyl and different methylene groups, which have previously been described in the literature on paint (Muizebelt et al. 1998; Muizebelt et al. 2000). The broad spectral feature for these resonances can be explained by the fact that a number of the methylene groups are neighbouring polar functional groups. The most intense response however arises from the presence of the inner CH_2 groups of the fatty acid chains that represent the bulk of the paint layer. During the 'drying' process of paint, referred to as autoxidation, oxygen from the air reacts with reactive methylene groups in the side chain of the triglyceride forming cross-links that eventually result in a chemically dried solidified layer. The functional groups that result from this process are ethers and peroxides that give the broad response between 50-100 ppm (upper trace). The small broad peak between 120-140 ppm results from residual double bonds that have not yet been consumed by the autoxidation. In a relatively young paint layer these resonances are still present, while it is expected that they will gradually disappear (see Figure 3). Finally, the resonances between 160-190 ppm are representative of carbon atoms related to carbonate found in the Lead White pigment and carbonyl groups from the esters of

Compound	Chemical shift / ppm
Cerussite	166.9 ^a
Hydrocerussite	167.8 ^a
Ester (triglyceride)	172-174 ^b
Stearic acid	180.5 ^c
Lead(II) acetate·3H ₂ O	180.1 ^d
Lead(II) acetate·½H ₂ O	180.2, 183.6, 187.6 ^d
Lead(II) azelate	183.9 ^a
Lead(II) carboxylate	181-186 ^a

Table 1. Carbonate and carbonyl ¹³C chemical shifts of compounds encountered in paint samples

^a this work,

^b (Mannina et al. 1999),

^c (Arata et al. 1999),

^d (Bryant et al. 1984)

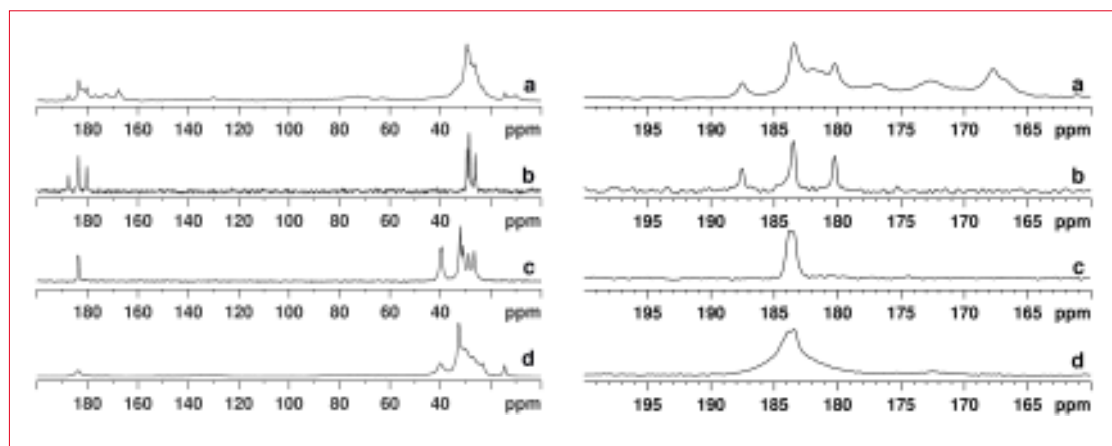


Fig. 1. ¹³C NMR spectra of a representative cured paint layer and three of important constituents. The left panel represents the full spectrum (0-200 ppm), while on the right an expansion of the carbonyl region (160-200 ppm) is shown. From top to bottom the following spectra are shown: (a) ZDAC 3 months cured (b) lead acetate hemi hydrate (c) lead azelate (d) artificial ionomeric network (see text) are shown.

the triglyceride and carboxylates in lead stearate. An expansion of the 160-190 ppm region is shown in the left panel of Figure 1. Table 1 sums up the resonances that can be found in this region.

Figure 1b shows the carbon spectrum of lead(II) acetate hemi hydrate. Lead acetate is an important paint additive that was generally used to increase the drying properties of paint (Carlyle 1991; Carlyle 2001). Recrystallisation of lead(II) acetate from water results in the well-known lead(II) acetate trihydrate (Bryant et al. 1984). It has been described that this compound readily releases part of its crystal water (Leibold and Huber 1980). Our research on the chemical properties of lead acetate has resulted in the determination of the novel structure of lead(II) acetate hemi hydrate by X-ray (Figure 2).

It appears that the compound with half a water molecule per molecule of lead acetate is the stable configuration at room temperature. It is proposed that the novel structure describes more accurately the lead acetate that 'sits on the shelf'. In the newly found crystal, 2 different co-ordination structures of the lead atom are found

with 4 unique acetates, which is reflected by the three resonances (ratio 1:2:1 see Table 1 and Figure 2) for both the methyl and COO⁻ moiety (Figure 1b). In the paint sample the lead acetate content is also clearly detected (Figure 1a, right panel). The carbon spectrum of lead(II) azelate is presented in Figure 1c. This compound is the most abundant of the diacids in aged oil paints and arises from the hydrolysis and oxidation of the cross-linked binding medium (Plater et al. 2003). Figure 1d shows the NMR response of a model compound that has been developed to describe the co-ordination of lead in the ionomeric network that arises after aging of the paint layer. The chemical structure of this model represents the cross-linked side chains of the oil without the glycerol unit that connects the side chains of the triglyceride oil molecules. After autoxidation, the ester bonds have been chemically hydrolysed resulting in free acid groups on the remaining structures. Subsequent reaction with a lead source resulted in a model of part of the postulated ionomeric network. The chemical shift of the resulting model at 183-184 ppm strongly resembles the response of lead azelate (Fig. 1d and e) and indicates that the presence of components of an ionomeric network can be identified by the (broad) NMR signal in this region.

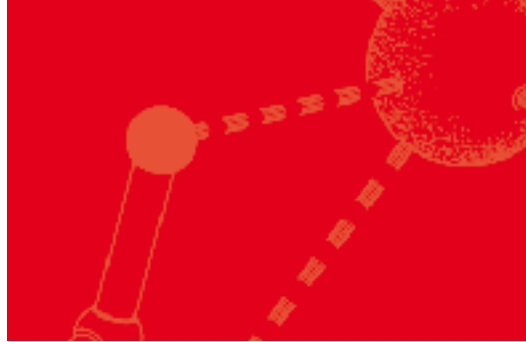


Figure 3 compares the ¹³C NMR spectra of samples that have been aged for 4 years with freshly prepared samples. Figure 3a shows oil ground with Lead White, while the Figure 3b is identical to the ZDAC sample in Figure 1a. Remarkably, the sample in Figure 3b shows, in addition to the lead acetate signal, the broad feature between 181-186 ppm that represents lead co-ordinated carboxylate structures. This indicates the formation of lead carboxylates at an early stage of the evolution of the paint layer. The source of these lead carboxylates could be the reaction between lead ions from the drier and carboxylates released during the preparation of the paint, however it could also indicate an early accelerated saponification of esters due to the presence of lead acetate, corroborating the catalytic role of lead acetate in the formation of long chain lead carboxylates (Carlyle 2000). Figure 3c shows the chemical shift response of sample ZDAC after 4 years. The most striking difference with the fresh ZDAC sample is the disappearance of the crystalline form of lead acetate and the increase of the lead carboxylates. A second observation is the decrease of double bonds in the ZDAC sample (120-140 ppm), which is even more apparent in the Figure 3d and 3e of the ZD paint samples, where the double bonds are virtually absent indicating the entire consumption of this functional group. The ester functionality of the triglycerides observed at 170-175 ppm remains largely unaffected at this stage. To our knowledge this is the first time that this final stage of drying of the binding medium is shown for a paint layer made with triglycerides. Figure 3d and 3e also show a further broadening of the signal around 183 ppm, which is assumed to arise as a consequence of a further penetration of lead atoms into the binding medium during the conversion to an ionomeric network. The only significant spectral difference between the last two traces is the absence of the small lead carbonate

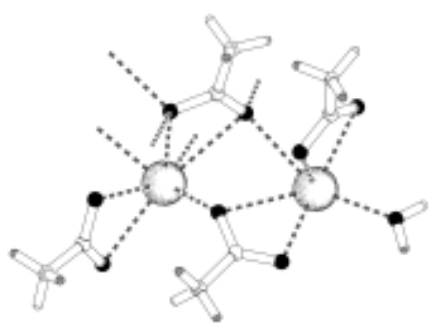


Fig. 2. Crystal structure of lead(II) acetate hemi hydrate. In the hemi hydrate structure one molecule of water is present for two molecules of lead acetate. The atoms are coded as follows: lead speckled, oxygen black, carbon white and hydrogen gray. The co-ordination of lead by oxygen atoms is indicated with the dotted lines.

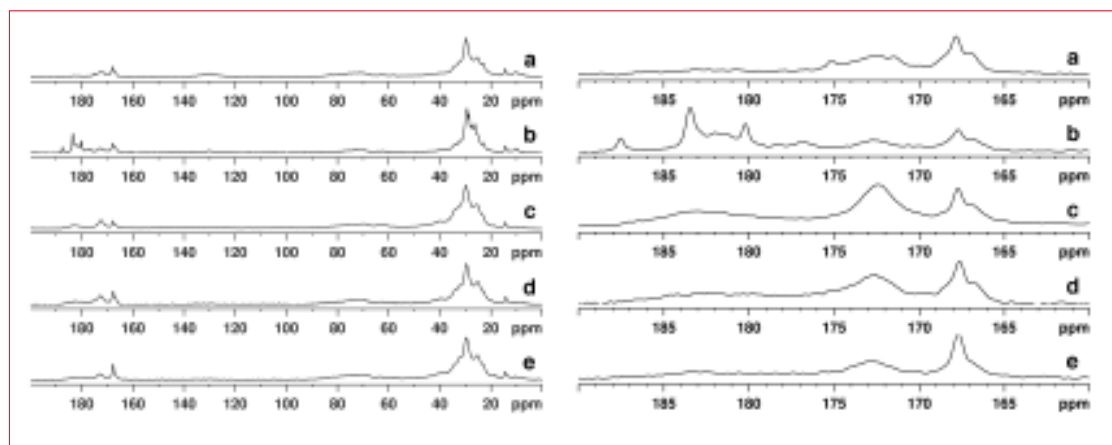


Fig. 3. ^{13}C NMR spectra of paint layers cured during different periods of time and under different conditions. The panel on left represents the full spectrum (0-200 ppm), while on the right an expansion of the carbonyl region (160-200 ppm) is shown. From top to bottom the following spectra are shown: (a) fresh oil ground with Lead White, 3 months cured (b) ZDAC, 3 months cured (c) ZDAC, 4 years old (d) ZD artificially aged, 4 years old (e) ZD kept at ambient condition, 4 years old.

peak at 167 ppm in the bottom spectrum. The decrease of the amount of lead carbonate seems to indicate an increasing alkalinity of the paint sample during ageing as has been suggested recently (Noble et al. 2002). Interestingly, this seems to occur under the influence of higher temperature and humidity since it is evident in a sample subjected to these conditions during artificial ageing. It was observed in GCMS experiments that the relative amount of saponification products increases after the exposure of paint layers to moisture (Keune 2005). These data fit in a growing body of evidence that the lead pigments are consumed by liberated acids in the paint layers. The free acid state is not apparent in the NMR experiments, which suggests that the free acid is only transiently present and reacts relatively rapid with the pigment. Recent results of the AMOLF group show that the reaction of acids with pigments in the solid state are fast even at room temperature and corroborate our observation (Hoogland and Boon 2006).

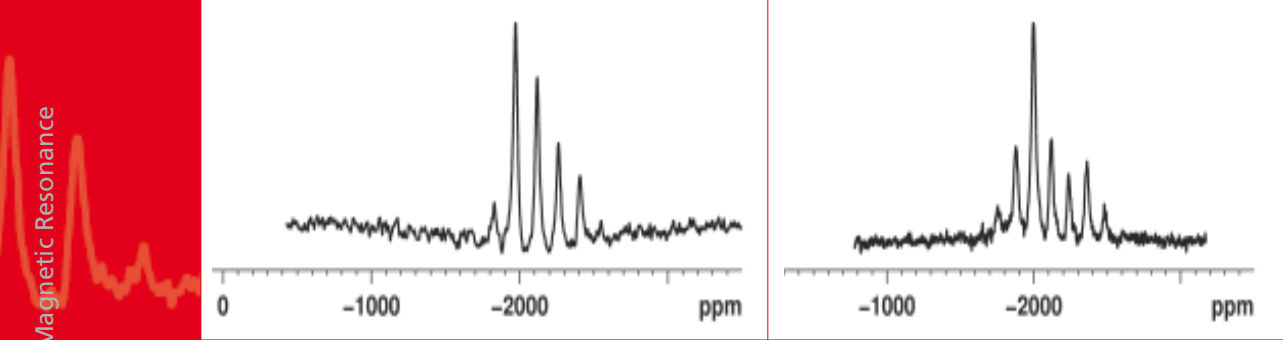


Fig. 4. ^{207}Pb NMR spectra of lead stearate (left panel) and lead azelate (right panel), the spectra are recorded at spinning frequencies of 12 and 11 kHz, respectively

Figure 4 shows the ^{207}Pb NMR spectra of lead(II) stearate and lead(II) azelate, in which an ensemble of evenly spaced peaks is observed. The ensemble arises as a consequence of macroscopic sample rotation (magic angle spinning), which is necessary to average the signal of different crystallite orientations. The observed signals represent the responses of single lead co-ordination sites corroborating previous results with X-ray Diffraction (Corbeil and Robinet 2002; Plater et al. 2003). Recording the spectra of the lead azelate and lead stearate under identical conditions results in lead-207 spectra that are very similar with respect to their isotropic chemical shift at -2135 ppm and to the width and asymmetry of the anisotropy. From a structural point of view this spectral resemblance is interesting because it indicates that the co-ordination of the lead atom in lead stearate, which crystal structure is unresolved to date, may be geometrically identical to the co-ordination structure in the lead azelate crystal structure. This observation is supported by the fact that the chemical shift of lead is extremely sensitive for small changes in the co-ordination shell (Gasque et al.). Unfortunately, the inability to distinguish between these two lead carboxylates also poses a complication in our effort to analyse paint samples with lead NMR, especially since both compounds take a paramount position in the current problem of the structure of traditional oil paint and its deterioration.

Hydrocerussite (Lead White) is another pivotal component in the study of paint deterioration, which was also studied by ^{207}Pb NMR. The crystal structure of hydrocerussite consists of 2 layers of lead carbonate alternating with a layer of lead hydroxide (Martinetto et al. 2002). While our experiments have shown that the NMR response of the lead carbonate layers of hydrocerussite corresponds to pure lead carbonate (cerussite), those experiments have been unable to reveal the signal of the lead hydroxide layer of the hydrocerussite lattice (data not shown). This is the case for both traditionally produced Lead White and hydrocerussite of which the purity was checked by X-ray. The detection problem in NMR may be explained by a strong reduction of the signal intensity due to two phenomena: (i) an extremely strong anisotropy of the chemical shift comparable to the ^{207}Pb spectrum of lead(II) acetate (Kye et al. 1999) and (ii) static disorder of the lead hydroxide lead site in the hydrocerussite lattice giving rise to additional dipolar line-broadening (Martinetto et al. 2002). In view of the fact that the observation of a number of compounds important to the problem of paint deterioration by means of ^{207}Pb NMR is not evident, it is concluded that future effort in the field of NMR on paint deterioration should be directed primarily on carbon NMR.

Conclusion

Based on the presented work it appears that the formation of the ionomeric network is starting in early stages of the evolution of the paint layer. It seems that the reaction between lead pigments and carboxylates as far as those have evolved is rapid and within 5 years after paint application the consumption of released carboxylates keeps the free acid concentration low. This implies that the formation of the ionomeric network consisting of lead ions and diacids as well as the process of phase separation leading to lead carboxylate aggregates may commence at an early stage. A systematic study comparing the same samples over the course of several years will give a more quantitative picture of the chemical processes. In addition, the study of paint samples from different eras could give better insight into the final composition. However at present the need for relative large amounts of sample to undertake NMR restricts its application to actual historic paint. Further work therefore will rely primarily on model systems and historically accurate reconstructions.

References

- Arata, S., Kurosu, H., Kuroki, S., Ando, I. (1999). Structural characterization of stearic acid in the crystalline state by the cross polarization in solid state C-13 NMR. *Journal of Molecular Structure* 513(1-3): 133-138.
- Bennet, A.E., Rienstra, C.M., Auger, M., Lakshmi, K.V., Griffin, R.G. (1995). *J. Chem. Phys.* 103: 6951-6958.
- Boon, J.J., Peulve, S.L., van den Brink, O.F., Duursma, M.C., Rainford, D. (1997). Molecular aspects of mobile and stationary phases in ageing tempera and oil paint films. In: *Early Italian Paintings: Techniques and Analysis* (E.T. Bakkenist, R. Hoppenbrouwers and H. Dubois, eds). Limburg Conservation Institute (SRAL), Maastricht. p. 35-56.
- Boon, J.J., Van der Weerd, J., Keune, K., Noble, P., Wadum, J. (2002). Mechanical and chemical changes in Old Master paintings: dissolution, metal soap formation and remineralization processes in lead pigmented ground/intermediate paint layers of 17th century paintings. *Proceedings of the ICOM-CC 13th Triennial Meeting in Rio de Janeiro Preprints* (R. Vontobel ed), James & James, London. p.401-406.
- Boon J.J., Gore E., Keune K., Burnstock A. (2005). Image analytical studies of lead soap aggregates and their relationship to lead and tin in 15th C lead tin yellow paints from the Sherbone triptych. In: *IRUG6 Conference 2004 Florence* (M. Picollo, ed), Il Prato, Padova, p. 66-74
- Boon J.J. (2006). Processes inside paintings that affect the picture: chemical changes at, near and underneath the paint surface. In *Reporting Highlights of the De Mayerne Programme* (J.J.Boon and E. Ferreira eds), this volume, p. 21-32
- Bryant, R.G., Chacko, V.P., Etter, M.C. (1984). 13C CPIMAS NMR and crystallographic investigation of the structure and solid-state transformations of lead(II) acetate trihydrate. *Inorganic Chemistry* 23: 3580-3584.
- Carlyle, L. (1991). A critical analysis of artists' handbooks, manuals and treatises on oil painting published in Britain between 1800-1900; with reference to selected eighteenth century sources, Ph.D. thesis. University of London, London.
- Carlyle, L. (2000). MOLART Fellowship Historical Reconstructions of Artists' Oil Paint: an investigation of oil processing methods and the use of medium modifiers. Report No. 72894, Canadian Conservation Institute, Ottawa.
- Carlyle, L. (2001). 'The artists' assistant': Oil painting instruction manuals and handbooks in Britain, 1800-1900. With references to selected eighteenth-century sources. Archetype Books, London.
- Corbeil, M.C., Robinet, L. (2002). X-ray powder diffraction data for selected metal soaps. Powder

- Diffraction* 17(1): 52-60.
- Fayon, F., Farnan, I., Bessada, C., Coutures, J., Massiot, D., Coutures, J. P. (1997). Empirical correlations between Pb-207 NMR chemical shifts and structure in solids. *Journal of the American Chemical Society* 119(29): 6837-6843.
 - Gasque, L., Verhoeven, M.A., Bernès, S., Barrios, F., Haasnoot, J.G., Reedijk, J.: manuscript in preparation.
 - Higgitt, C., Spring, M., Saunders, D. (2003). Pigment-medium interactions in oil paint films containing read lead and lead-tin yellow. *National Gallery Technical Bulletin* 24: 75-95.
 - Hoogland, F., Boon, J.J. (2006). Unpublished. Reported at the ICOMCC Scientific Research Working Group interim meeting on lead soaps in collaboration with MaSC held in the Van Gogh museum in Amsterdam on 10 september 2005. See also Boon (2006) this volume fig. 2.
 - Keune, K. (2005). Binding medium, pigments and metal soap characterised and localised in paint cross sections. Ph.D. Thesis University of Amsterdam, Amsterdam. MOLART Report 11, Amolf, Amsterdam
 - Kye, Y.S., Connolly, S., Herreros, B., Harbison, G.S. (1999). Pb-207 solid state NMR studies of lead compounds. *Main Group Metal Chemistry* 22(6): 373-383.
 - Leibold, R., Huber, F. (1980). Thermal-Decomposition of Lead(II) Acetate. *Journal of Thermal Analysis* 18(3): 493-500.
 - Mallegol, J., Gardette, J.L., Lemaire, J. (1999). Long-term behavior of oil-based varnishes and paints I. Spectroscopic analysis of curing drying oils. *Journal of the American Oil Chemists Society* 76(8): 967-976.
 - Mallegol, J., Gardette, J.L., Lemaire, J. (2000). Long-term behavior of oil-based varnishes and paints. Photo- and thermooxidation of cured linseed oil. *Journal of the American Oil Chemists Society* 77(3): 257-263.
 - Mannina, L., Luchinat, C., Emanuele, M.C., Segre, A. (1999). Acyl positional distribution of glycerol tri-esters in vegetable oils: a C-13 NMR study. *Chemistry and Physics of Lipids* 103(1-2): 47-55.
 - Martinetto, P., Anne, M., Dooryhee, E., Walter, P., Tsoucaris, G. (2002). Synthetic hydrocerussite, 2PbCO(3). Pb(OH)(2), by X-ray powder diffraction. *Acta Crystallographica Section C-Crystal Structure Communications* 58: 182-184.
 - Metz, G., Wu, X., Smith, S.O. (1994). *J. Magn. Reson.* A110: 219-227.
 - Muizebelt, W.J., Donkerbroek, J.J., Nielen, M.W.F., Hussem, J.B., Biemond, M.E.F., Klaasen, R.P., Zabel, K.H. (1998). Oxidative cross-linking of alkyd resins studied with mass spectrometry and NMR using model compounds. *Journal of Coatings Technology* 70(876): 83-93.
 - Muizebelt, W.J., Hubert, J.C., Nielen, M.W.F., Klaasen, R.P., Zabel, K.H. (2000). Crosslink mechanisms of high-solids alkyd resins in the presence of reactive diluents. *Progress in Organic Coatings* 40(1-4): 121-130.
 - Noble, P., Boon, J.J., Wadum, J. (2002). Dissolution, aggregation and protrusion, Lead soap formation in 17th century grounds and paint layers. *Artmatters* 1, p.46-61.
 - Noble, P., Van Loon, A., Boon, J.J. (2005). Chemical changes in Old Master paintings II: darkening due to increased transparency as a result of metal soap formation. *Proceedings of 14th Triennial ICOM-CC Meeting in The Hague* (I. Verger ed), James & James, London. p. 496-503.
 - Parella, T. (1998). NMR Periodic Table <http://www.brucker.de/guide/el/eNMR/chem/NMRnuclei.html>.
 - Plater, M. J., De Silva, B., Gelbrich, T., Hursthouse, M.B., Higgitt, C.L., Saunders, D.R. (2003). The characterisation of lead fatty acid soaps in 'protrusions' in aged traditional oil paint. *Polyhedron* 22(24): 3171-3179.
 - Tarbutton, G., Vosburgh, W.C. (1932). The system lead acetate, acetate, water. *Journal of the American Chemical Society* 54: 4537-4544.
 - Van den Berg, J.D.J., Van den Berg, K.J., Boon, J.J. (2001). Determination of the degree of hydrolysis of oil paint samples using a two-step derivatisation method and on-column GC/MS. *Progress in Organic Coatings* 41(1-3): 143-155.
 - van der Weerd, J., Boon, J.J., Geldof, M., Heeren, R.A., Noble, P. (2001). Chemical changes in Old Master paintings: dissolution, metal soap formation and remineralization processes in lead pigmented paint layers of 17th century paintings. *Zeitschrift für Kunsttechnologie und Konservierung* 16(1): 36-51.
 - Warzeska, S.T., Zonneveld, M., Van Gorkum, R., Muizebelt, W.J., Bouwman, E., Reedijk, J. (2002). The influence of bipyridine on the drying of alkyd paints: a model. *Progress in Organic Coatings* 44: 243-248.

On metal soap related colour and transparency changes in a 19th C painting by Millais

THE INFLUENCE OF PAINTING METHODS AND MATERIALS ON THE PRESENT APPEARANCE OF 19TH C PAINTINGS (MM19)

Abstract:

The painting '*Speak! Speak!*' by J.E. Millais at the Tate Gallery shows severe loss of detail in certain areas apparently as a consequence of paint darkening. This partial darkening is suspected to be due to the loss of opacity of white paints associated with the saponification of the white pigments. This optical effect has recently been demonstrated in lead white containing areas in 17th Century paintings (Noble *et al.* 2005; Keune 2005). Analytical microscopic data have indeed shown the extensive saponification of the top lead white and zinc white containing paint layers, with evidence of the formation of aggregates of zinc carboxylates. As a consequence the light scattering properties and opacity of the top layers are reduced, allowing the underpaint layers to become more prominent. The apparent degree of darkening of the paint areas are not only dependent on the degree of saponification of the top layer but also has a relation with the colour of the affected paint layer and the paint underneath.

¹ Netherlands Institute for Cultural Heritage, P.O. Box 76709, 1070 KA Amsterdam, The Netherlands
Yoshiko.Shimadzu@icn.nl, Klaas.Jan.vd.Berg@icn.nl

Introduction

The De Mayerne project MM19 on transparency and darkening in 19th Century paints started in 2004 building on an earlier 19th Century research project, which was a collaborative effort between the ICN, Dutch museums and AMOLF. The latter project comprised a study on presumably darkened paintings from Dutch and French 19th and early 20th century artists. Darkening in the paintings studied often appeared to be related to initially transparent and medium rich paints. Paint deformations were found to be more related to the painting technique than the materials used (van den Berg *et al.*, 2002; van den Berg, 2003).

The MM19 builds on these results by further investigating the factors that influence the appearance of 19th C paintings. Particular emphasis is given to colour change phenomena such as darkening of paints resulting from medium discoloration, increased transparency and the fading of pigments. This is done by technical examination of the picture, the study of surviving tube paints and palettes as well as by analysis of paint samples using analytical microscopy and mass spectrometric techniques. The resulting hypotheses are tested by preparation of paint reconstructions supported by relevant documentary sources.

The present paper highlights the influence of the dissolution of white pigments on the darkening of the picture.

Transparency change and darkening

Oil paints can become more translucent with time and may reveal underpaint layers to a degree that it exposes the underdrawing and even the artists' *pentimento* (Kühn, 1963; Laurie, 1967 and Van Eikema Hommes, 2004). This has been interpreted as a darkening of the painting as well as a change in intent and appearance of the picture. Explanations for the phenomenon have been suggested in the early literature: increasing transparency in oil paintings would be caused by the "saponification of lead white pigment" as suggested by Eibner (1909) or as alteration of the refractive index of the oil media (Laurie, 1926). Townsend (1993) pointed out that a refractive index change of the oil binding medium is in fact small and unlikely to have any influence in the appearance of paintings, which rejects Laurie's proposed explanation. Support for the first hypothesis is found in the many recent reports on lead soap formation and aggregation (Boon *et al.* 2002; Noble *et al.* 2002; Higgitt *et al.* 2004; Boon *et al.* 2005, Keune 2005; Noble *et al.* 2005), the observed dissolution of lead white in underpaints (Keune 2005) and the changes in transparency in a panel painting of Van der Neer (Noble *et al.* 2005). In the latter painting specific areas in the painting have a darker appearance, which is related to a severe loss of light reflectivity due to replacement of lead white by lead soaps as a function of the thickness of the ground and the nature of the wood underneath.

The saponification of lead white, red lead, and zinc oxide in oil paint has been described in the paint industry literature in the beginning of 20th century. Although these pigments were considered to be beneficial for the rheology and drying properties of the industrial paint (Heaton, 1928; Tumsa and Mecklenburg, 2005), they were often associated with a surface haziness called 'seeding' (Jacobsen and Gardner, 1941; Elm, 1957). This defect was thought to result from the reaction of the



Fig. 1. *Speak! Speak!* (1895) by John Everett Millais (Tate). Inv. nr. N01584.

acid components in oil with the basic pigments. A similar phenomenon was also observed in oil paintings a short while after drying (Ordonez and Twilley, 1997). Lead and zinc soaps have been identified as aggregates in paint layers of 17th and 19th C paintings in investigated with support of the MOLART and the De Mayerne research programme (Van der Weerd, 2002; Keune, 2005). These studies have shown that the saponification of lead and zinc containing oil paints is not uncommon. The chapters by Verhoeven et al. (2006) and Boon (2006) in this volume point out that the interaction of metals from pigments and driers with compounds derived from the oxidation of oil, form an essential part of the development into a stable polymer network in paints. On the other hand, especially monocarboxylic acids can develop into metal soap aggregates that may threaten the stability of the painting. Not all the paints containing the pigments mentioned have developed the surface efflorescence observed as haziness nor alteration in paint appearance. Our MM19 project focuses on a more systematic investigation of the relationship between the saponification of the white pigments and alterations in the appearance of the picture.

Scientific examinations of the painting

The samples

The painting '*Speak! Speak!*' in 1895 by John Everett Millais (Tate, Inv. nr. N01584) (Fig. 1) that shows partial darkening, was examined. The focus area was the white and yellow fur cover in the foreground painted over the dark shadows under the bed. A paint sample (s17) was taken from this area. Another sample (s16) was removed from the woman's white dress for comparison (Fig. 2). In this area no significant darkening is observed. As the painting is a night scene, everything is illuminated by candlelight. Flesh-toned paint is hardly present anywhere. For example the man's skin



Fig. 2. Sampling areas in *Speak! Speak!* (1895) (Tate). Sample s16 was taken from the white dress of the standing woman, whereas sample s17 was taken from the yellow fur cover over the bed shadow.

is depicted in an opaque orange paint to reflect the candlelit environment. In addition, many of the warm-toned brown areas include the same opaque orange pigment. Any change in the lighter toned paint components would therefore lead to a darker appearance.

Methodology of scientific examinations

Paint cross sections were examined with a ZEISS Axioplan 2 light microscope at ICN, and Fourier transform infrared spectrometry imaging technique (img-FTIR) was performed by Bio-Rad FTS-6000 FTIR spectrometer connected to an IR microscope Bio-Rad UMA-500 at AMOLF. This technique is particularly useful in the identification and localisation of metal soaps in cross sections through the characteristic absorption at around 1530 cm^{-1} by metal-carboxylate group. Further study of the layer structure, the identification and distribution of elements was performed with a JEOL JSM-5910LV scanning electron microscope (SEM) using a backscattered electron (BSE) detector and a detector for an energy dispersive x-ray analysis (EDX) provided by the ThermoNoran operated by the Vantage software.

Results and discussion

The layer build-up was examined by light microscopy and scanning electron microscopy (SEM) in backscatter electron detection mode. It was observed that both sample s16 and s17 have a common build-up of the priming: a white layer under a light brown priming layer (layers 1 and 2 in figs 3 and 4). The first priming layer (layer 1) contains calcium carbonate and lead white whereas the second (layer 2) is a lead white containing paint layer tinted with red ochre.

In the sample collected from the white dress (s16), a very thin layer 3 with lead white, umber and bone black was applied after the priming. On top of it, two thin layers;

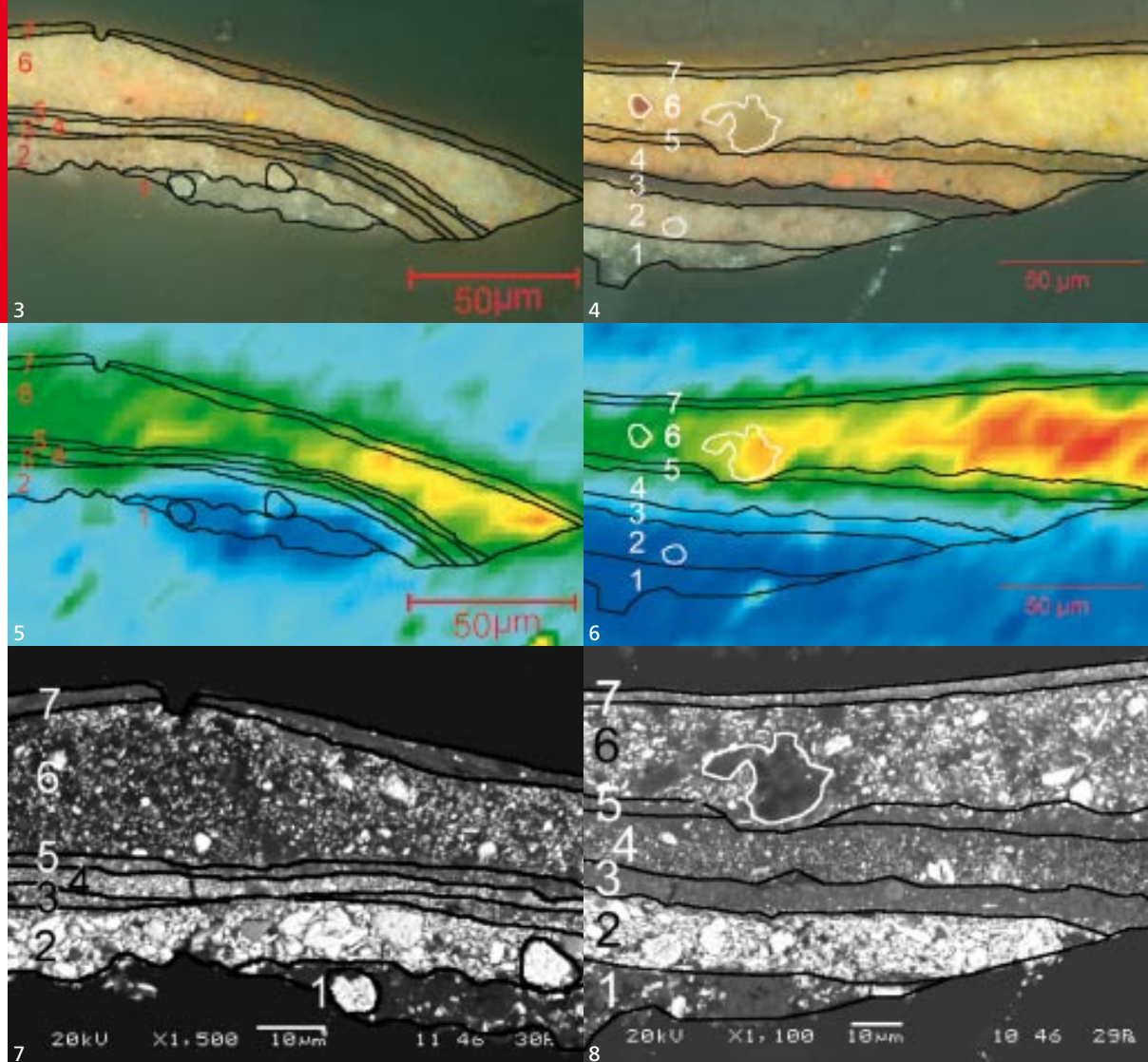


Fig. 3. Light microscopic image of s16 cross-section from the white dress showing seven layers.

Fig. 4. Light microscopic image of s17 cross-section from the yellow fur showing seven layers.

Fig. 5. Infrared absorption image at 1531 cm^{-1} representing metal carboxylate absorption in s16, indicating the high absorption in layer 6 (Red-yellow-green-blue corresponding high to low intensity in order)

Fig. 6. Infrared absorption image at 1530 cm^{-1} representing metal carboxylate absorption in s17, indicating the high absorption in layer 6.

Fig. 7. SEM back-scattered image of s16 showing low BSE density in layer 6 supporting the presence of metal soaps

Fig. 8. SEM back-scattered image of s17 showing a metal soap aggregate as a dark spot in layer 6

layer 4 with lead white and bone black, and layer 5 with a similar formulation to layer 3, are observed. The layer 6 contains lead white, vermilion and chrome yellow. EDX analysis detected zinc in this layer suggesting the use of zinc oxide. Finally, a translucent brown glaze, is thinly applied presumably to obtain a “candle-lit” atmosphere (layer 7, Fig.3, Table 1). This thin glaze will not have significant hiding power and the surface appearance of this area is in part due to layer 6.

Table 1. Layer build-up and identified pigments in s16

Layer No	Appearance in cross section	Identified pigments
7	Thinly applied brown glaze	lead white, red ochre
6	Reddish white	lead white, zinc oxide, vermilion, Al substrate (Red lakes?!), chrome yellow,
5	translucent light brown	umber, lead white
4	grey	lead white, bone black
3	translucent light brown	lead white, umber, bone black
2	brown second priming	lead white, red ochre, barites
1	white first priming	calcium carbonate, lead white

Table 2. Layer build-up and identified pigments in s17

Layer No	Appearance in cross section	Identified pigments
7	Thinly applied brown glaze	lead white, red ochre
6	orange-yellow	lead white, zinc oxide, chrome yellow, vermilion, red ochre
5	translucent yellow layer	(oiling out?)
4	red	lead white, vermilion, bone black
3	dark brown	umber, lead white
2	brown second priming	lead white, red ochre, barites
1	white first priming	calcium carbonate, lead white

Sample s17 has a dark brown paint (layer 3) containing umber and lead white, on top of the second priming. The subsequent layer 4 contains lead white, vermilion and bone black. There are few pigment particles in layer 5 which could be interpreted as an oiling out layer. The layer 6 corresponds to the light yellow paint depicting the fur cover, which consists mainly of chrome yellow, lead white, and zinc oxide (Fig. 4., Table 2).

Identification and localisation of metal soaps in the cross-sections were performed by the FTIR microscopy by imaging the metal carboxylate absorption peak at around 1530 cm^{-1} . The carboxylate absorption from zinc carboxylates appears at 1550 cm^{-1} to 1530 cm^{-1} , whereas lead carboxylates appears at 1540 cm^{-1} to 1510 cm^{-1} . The distinction of zinc carboxylates from lead carboxylates, therefore, is uncertain on the basis of FTIR data only. The SEM-EDX examination is useful in this respect as it provides the location of the elements of zinc and lead. It was established that metal carboxylates are present in layer 6 of sample s16 (Fig. 5), and also in layer 6 of sample s17 (Fig. 6). The intense absorption indicated as red and yellow areas in Fig. 5 and 6 correspond to translucent area in the light microscope images (Fig. 3, 4) thus supporting the formation of metal soaps (Keune, 2005; Higgitt *et al.*, 2003).

The SEM backscattered electron images of s16 and s17 also show a lower BSE density of the layers 6 in both cross sections (Figs 7 and 8). In general, lead white pigments in paint layer appear bright in SEM backscattered images [see for example the lead white pigment particles in layer 2 of s17 (Fig. 8)]. In contrast metal soaps appear darker due to their low degree of crystallinity and higher organic content (Keune, 2005). These dark areas in the SEM images overlap with areas that have a semi translucent appearance in light microscope (Figs 4 and 8) and are rich in metal carboxylates according to the imaging FTIR results (Fig. 6). The edges of the pigment particles are not very well defined and suggest an interface area where the reaction

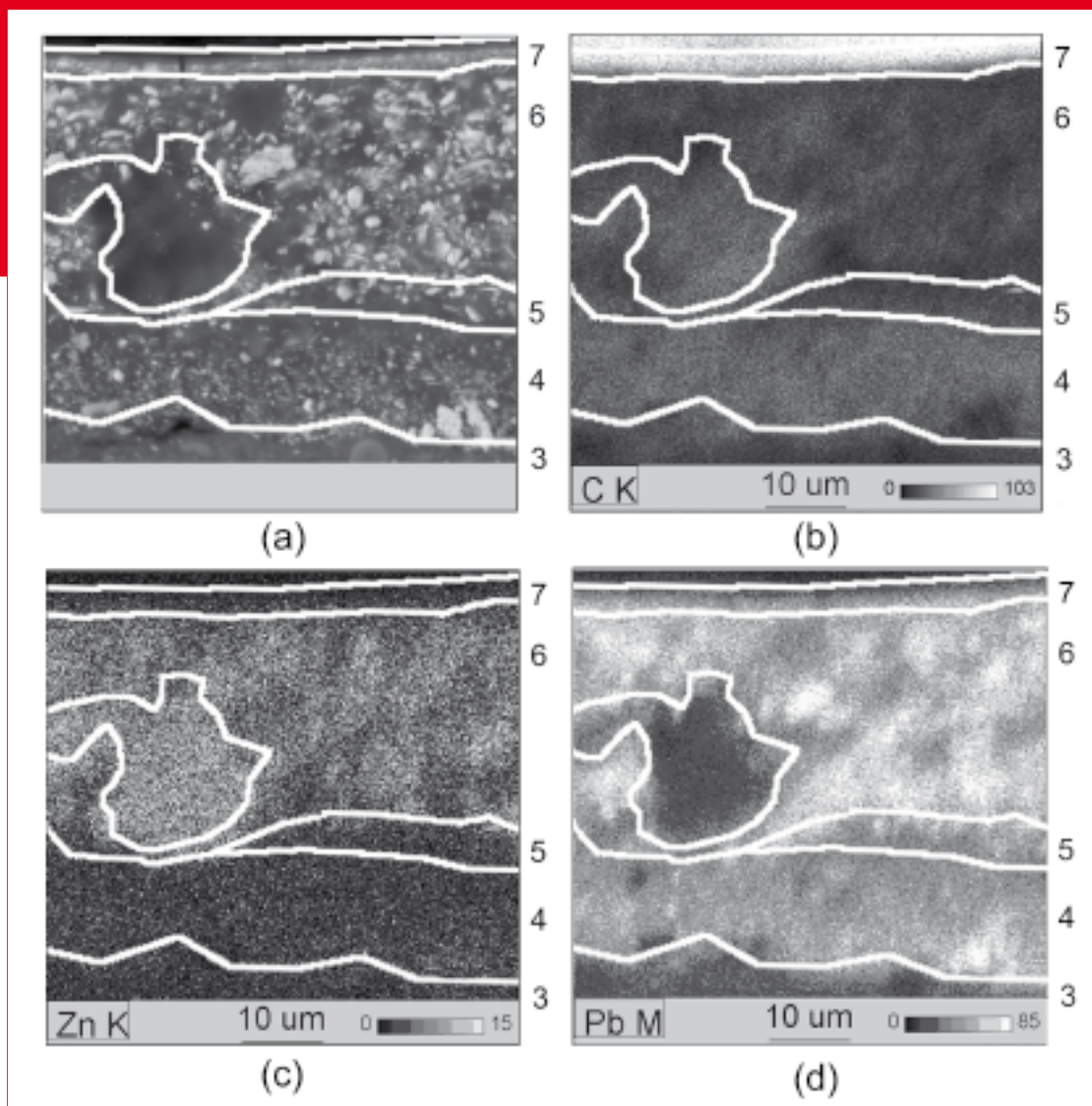


Fig. 9. EDX mapping of s17 showing the elements distribution

- (a) SEM back scattered image of analysed area.
- (b) Mapping of carbon distribution showing relative high concentration of carbon in the marked area, layer 6.
- (c) Mapping of zinc distribution showing zinc is mainly in layer 6.
- (d) Mapping of lead distribution showing lead is in layer 6 as well as in layer 4 and 5.

between the binding medium and pigment has occurred, further supporting the formation of metal soaps.

Interestingly, the sample s16 and s17 both have other lead white containing layers where there is the potential for lead soap formation, but metal soaps were only found in the upper layers. A crucial difference between metal soap containing layers and those that show no evidence of metal soap formation is the presence of zinc.



The EDX mapping of sample s17 reveals that a relatively higher amount of zinc was detected in the layer 6 which shows a high intensity of metal carboxylate absorption. The dark area indeed is rich in carbon and zinc (Fig. 9).

Although the dark spots, especially the marked area in layer 6 seem to be mainly consisting of zinc soap according to the EDX data, we cannot exclude the presence of lead in these agglomerates. According to recent studies, it seems that free monocarboxylic acids from hydrolysis of acylglycerol moieties in oil paint is required for the saponification of lead white (Hoogland and Boon, 2006). Further, it has been reported that zinc oxide paint has high moisture sorption behaviour (Dunn, 1954). Therefore, it is reasonable to assume that zinc oxide containing paints would be more reactive than those with lead white only since the capacity of moisture sorption could increase the hydrolysis of the oil network in the paint and thus lead to subsequent saponification of zinc and lead pigments.

The most significant optical effect of saponification is the partial disappearance of the white pigments particles. As pigment particles are good light reflectors (Hunter, 1975), a loss of the particle surface resulting from the interaction between medium and pigment, would decrease total light reflectance. This allows the incident light to transmit through the upper layers and reach the lower paint layers. In other words it results in a relative increase of light absorption, i.e. a decrease in reflected light and as a consequence one expects an optical darkening, especially when upper paints are lighter than underlying paints. It is evident in the study of '*Speak! Speak!*', where both samples collected from a darkened area (s17) and from an apparently optically unaltered area (s16) are highly saponified. Here only the s17 has darker paints underneath as well as a high amount of chrome yellow in the upper layer therefore it develops a darker appearance upon dissolution of the white pigments. .

Conclusions

The combination of chemical analysis and detailed examination of the darkened areas in *Speak! Speak!* demonstrates that the relative light absorption of surface paint layers is increased due to saponification of white pigments. The overall effect causes a darkening of the painting. On the other hand, saponification by itself might not produce an appreciable optical darkening effect. The critical factor is the colour of the remaining paint and on the colour of the underlying paint as was demonstrated here. The presence of zinc white seems to more actively promote the saponification compared to lead white alone because of its zinc white's hygroscopicity. This aspect will be further investigated.

Acknowledgments

Dr E.S.B. Ferreira at AMOLF is gratefully acknowledged for assistance with data processing and writing of the paper. We thank Ferreira and Boon for extensive editing of the paper. We also thank Townsend (Tate) and Tate for access to the painting and provision of samples. Boon (AMOLF), Townsend (Tate), L. Carlyle (ICN and Tate) and Burnstock (Courtauld) are acknowledged for helpful discussions in the course of the project. We acknowledge the support from our colleagues at ICN and AMOLF. The facilities at AMOLF are supported by FOM via FOM programme 49 and the De Mayerne Project MOLMAP both supported financially by NWO, The Hague.

References

- Boon, J. J., Van der Weerd, J., Keune, K., Noble, P., Wadum, J. (2002). *Mechanical and chemical changes in Old Master paintings: dissolution, metal soap formation and remineralization processes in lead pigmented ground/intermediate paint layers of 17th century paintings*. Proceedings of the ICOM-CC 13th Triennial Meeting in Rio de Janeiro Preprints (R. Vontobel ed), James & James, London. p.401-406.
- Boon J.J., Gore E., Keune K., Burnstock A. (2005). *Image analytical studies of lead soap aggregates and their relationship to lead and tin in 15th C lead tin yellow paints from the Sherbone triptych*. In: IRUG6 Conference 2004 Florence (M. Pi-
collo, ed), Il Prato, Padova, p. 66-74
- Boon J.J. (2006). *Processes inside paintings that affect the picture: chemical changes at, near and underneath the paint surface*. In: Reporting Highlights of the De Mayerne Programme (J.J.Boon and E. Ferreira eds), this volume, p. 21-32
- Eibner A., (1909). *Malmateri- alienkunde –als Grundlage der Maltechnik*. Verlag von Julius Springer, Berlin, p-121.
- Elm A.C., (1957). *Reevaluation of the Function of Pigments in Paints*. Official Digest, 20, 351-385.
- Dunn, Jr E.J., (1954). *Moisture Resistance of Paint Films*. Official Digest, 26, 387-407.
- Heaton N., (1928). *Outlines of paint technology*. Charles Griggin & Company, Limited, London, p-80.
- Higgitt C. et. al. (200). *Pigment-medium Interactions in Oil Paint Films containing Red Lead or Lead-tin Yellow*. National Gallery Technical Bulletin, 24, 75-95.
- Hoogland, F., Boon, J. J. (2006). *Unpublished*. Reported at the ICOMCC Scientific Research Working Group interim meeting on lead soaps in collaboration with MaSC held in the Van Gogh museum in Amsterdam on 10 september 2005.
- Hunter R.S., (1975). *The Measurement of Appearance*. John Wiley & Sons, Inc., Toronto, pp.30-33.
- Jacobsen A.E. and Gardner W.H., (1941). *Zinc Soaps in Paints: zinc oleates*. Industrial and Engineering Chemistry, 33, 1254-1256.
- Keune K., (2005). *Binding medium, pigments and metal soaps characterized and localized in paint cross-*

- sections. PhD Thesis. University of Amsterdam, Amsterdam, The Netherlands, pp.113-169.
- Kühn, H., (1963). *Aspects of Panel-Painting*, Ciba review, 1, 3-36.
 - Laurie A.P., (1926). *On the Change of Refractive Index of Linseed Oil in the Process of Drying and its Effect on the Deterioration of Oil Paintings*. Proceedings of the Royal Society of London, 112, 176-181.
 - Laurie, A.P., (1967). *The Painter's Methods and Materials*, Dover Publications, New York, pp.140-155.
 - Noble, P., Boon, J. J., Wadum, J. (2002). *Dissolution, aggregation and protrusion, Lead soap formation in 17th century grounds and paint layers*. Artmatters1, p.46-61.
 - Noble P. et al., (2005). *Chemical changes in old master paintings II: darkening due to increased transparency as a result of metal soap formation*. In: *The ICOM Committee for Conservation, the 14th Triennial Meeting, Den Haag, part I*, pp.496-503.
 - Ordonez E. and Twilley J. (1997). *Clarifying the Haze; Efflorescence on Works of Art*. Analytical chemistry, 69, 416A-422A.
 - Townsend J.H. (1993). *The refractive index of 19th-Century paint Media: A preliminary study*. In: *ICOM Committee for Conservation 10th Triennial Meeting*. Washington, DC, 22 -27 September 1993, pp.586-592.
 - Tumosa C.S. and Mecklenburg M.F., (2005). *The influence of lead ions on the drying of oils*. *Reviews in conservation*, 6, 39-47.
 - Van den Berg K.J., Geldof M., de Groot S., van Keulen H. (2002). *Darkening and surface degradation in 19th- and early 20th century paintings an analytical study*. In: *ICOM Committee for Conservation 13th Triennial Meeting*. Rio de Janeiro, 22 -28 September 2002, p. 464-472.
 - Van den Berg K.J., (2003), *Colour changes in nineteenth century paintings*. In: *A multidisciplinary NWO PRIORITEIT project On Molecular Aspects of Ageing in Painted Works of Art. Final report and highlights 1995-2002* (Clarke M. and Boon J., eds), FOM Institute AMOLF, Amsterdam, p. 68.
 - Van der Weerd J., (2002). *Micro-spectroscopic analysis of traditional oil paint*. PhD Thesis. University of Amsterdam, Amsterdam, The Netherlands.
 - Van Eikema Hommes M., (2004). *Changing Pictures –Discolouration in 15th to 17th Century Oil Paintings*. Archetype Publications Ltd., London, p-38.
 - Michiel A. Verhoeven M.A., Carlyle L., Reedijk J., and Haasnoot J.G., (2006). *Exploring the application of solid-state Nuclear Magnetic Resonance to the study of the deterioration of paintings*. In *Reporting Highlights of the De Mayerne Programme* (J.J.Boon and E. Ferreira eds), this volume, p. 33-42.

Chemical Characterisation of thin intermediate layers: Case study of a sample from the 15th century painting, *The Descent from the Cross* by Rogier van der Weyden.

INFRARED REFLECTOGRAPHY: EVALUATIVE STUDIES

Abstract:

A combination of analytical microscopic techniques, which includes light microscopy (LM), Scanning electron microscopy equipped with electron diffraction X-ray detection (SEM-EDX), Secondary Ion Mass Spectrometry (SIMS) and imaging FTIR were applied to study preparatory layers and in particular thin intermediate layers.

The preparatory layers of the 15th century panel painting *The Descent from the Cross* by Rogier van der Weyden was investigated in a cross section taken from the virgin's blue robe. High magnification SEM and nano-SIMS are reported here.

The isolation or intermediate layer is characterised by the higher concentration of carbon in comparison to the adjacent layers, interpreted as being richer in organic binding medium. SIMS data suggests the presence of oleaginous binding media. Nano-SIMS gives no indication of the presence of proteins suggesting the medium is not an emulsion. Only a few lead white particles are found in the layer. However SEM EDX mapping shows that the lead is also finely dispersed in the layer and not only associated with the lead white particles. There is little indication of lead or oil medium penetration in the ground. These results show that the isolation or intermediate layer has the chemical characteristics of a leaded oil with gel like properties. This conclusion is in line with the observations made by Brinkman (1993) on the properties of intermediate layers and is supported by the comparative re-examination of his reconstructions after 26 years of ageing under ambient conditions.

¹ Current address: Schweizerisches Institut für Kunstwissenschaft, Zollikerstrasse 32, CH - 8032 Zürich ester.ferreira@sikart.ch

² Courtauld Institute of Art, Somerset House, Strand, London, WC2R 0RN, UK

³ FOM Institute-AMOLF, Kruislaan 407, NL-1098 SJ Amsterdam, keune@amolf.nl, boon@amolf.nl

Introduction

The function and composition of intermediate preparatory layers, including underdrawing and isolation layers, is often a source of debate in the field of historical art technology and conservation (Kirby *et al.*, 2002). Significant analytical challenges are present because these layers are extremely thin and intercalated between the priming or ground and the paint layer. The composition of preparatory layers, their location and their function in a multi-layered paint system, in particular in the case of the Flemish primitive painters, has been a recent focus of the Molecular Painting Studies group at AMOLF FOM. The De Mayerne project "IRR Evaluative studies" gave the opportunity to apply several imaging analytical spectroscopic techniques to this problem.

A paint sample including the preparatory layers taken from the virgin's blue robe from the 15th Century panel painting *The Descent from the Cross* by Rogier van der Weyden (1399-1464) was one of the samples selected for this study. The painting and the chemical characterisation the paint sample has been described before (van Asperen de Boer *et al.*, 1992; Keune *et al.*, 2004). Van Asperen de Boer *et al.*, (1992) gave a description of the build up of the preparatory layers of this painting as an off-white ground layer, a black layer representing the underdrawing and a thin brownish-white layer with red and black particles (about 9 μm thick). It is proposed that the underdrawing consists of an aqueous black ink applied with a thin brush.

The chemical characterisation of the paint layers of this sample concentrates in a non-destructive manner on the examination of the nature and distribution of pigments, binding media as well as their chemical interaction (Keune *et al.*, 2004). In that study, the potential of SIMS, as a new technique for the examination of paint cross-sections, in combination with light microscopic, imaging-FTIR and SEM/EDX data is demonstrated. The light microscopic picture of the cross-section (Fig. 1) shows preparatory layers that consist of a thick ground layer (168-186 μm) (layer 1), a very thin brownish-black underdrawing layer (1-2 μm , layer 2) and a thin light brown intermediate layer with black and red particles (6 μm , layer 3). Further description of the remaining paint layers can be found elsewhere (Keune *et al.*, 2004).

The analysis of this cross-section was recently taken further and the new high magnification SEM and nano-SIMS results reported here relate to the characterisation of the preparatory layers, in particular the extremely thin underdrawing and intermediate layers (layers 2 and 3).

Preparatory layers

The unknown nature of the media used to formulate preparatory layers has been a topic of discussion in art technological history and the conservation field as preparatory layers have an important role to play in the stability of the paint. Preparatory layers include the ground, the underdrawing and intermediate, isolation or *imprimatura* layers. Traditionally in Northern European Renaissance painting the ground layers was composed of chalk (calcium carbonate) and glue, whereas in Southern European tradition it is often composed of gypsum (calcium sulphate) and glue. The underdrawing is also considered a preparatory layer. Often a thin,

transparent intermediate layer applied either directly to the ground or over the underdrawing is observed. The function of this layer can be multiple and if applied directly to the ground, it will reduce its absorbency although its function can also be that of fixating the underdrawing to prevent it from being picked up by the brush. The nomenclature applied to these layers is based in the interpretation of their function. So for our purposes we shall define it as intermediate layer.

There are only limited number of chemical analysis reported of the composition of intermediate layers. A few examples will be summarised in the following paragraphs.

Northern European workshops

In paintings from early Netherlandish workshops the intermediate layer has mainly been described as a thin, translucent, medium rich layer containing drying oil but rarely the identification of the media is backed up with chemical analytical data. It was observed in a thorough survey of early Netherlandish panel paintings, (Campbell *et al.*, 1997) that a thin intermediate layer containing lead white was frequently applied over the chalk ground to function as isolation layer of the ground and to decrease the absorption of oil from the paint. This intermediate layer was found to contain drying oil and it is postulated that this is generally the case, especially when only drying oil media are found in the paint layers. The intermediate layers are described as being extremely medium rich and to have low pigment content. Brinkman *et al.* (1984) re-examined cross sections made from the "Het Lam Gods" retable of van Eyck with special attention for the ground, underdrawing, isolation and other preparatory layers (see also Brinkman, 1993). Light microscopy showed a transparent yellow brown isolation layer of 5-15 micron assessed to be an oil based substance intended to prevent excessive absorption of oil into the ground. Electron microprobe profiling of this isolation layer by Brinkman and co-workers demonstrated a relatively high abundance of lead, while lead was absent in the ground and the overlying adjacent paint layers (5 samples tested). Reconstructions demonstrated that only a leaded oil (linseed oil boiled for 2 hours in the presence of litharge) showed the physical characteristics that were observed in the painting. Brinkman (1993) concludes that Van Eyck used a lead treated oil for his isolation layers.

Paintings by Rogier van der Weyden

The *imprimatura*/intermediate layer of four paintings by Rogier van der Weyden or from his workshop have been described in literature (Campbell *et al.*, 1997a). On the *Magdalen Reading* and *the Exhumation of Saint Hubert* a light grey *imprimatura*/intermediate layer can be detected by light microscopic analysis of the cross-sections. These layers contain lead white and a low quantity of carbon black particles. In the case of *Saint Ivo* only lead white is present and in the case of the *Pietà* in addition to the lead white pigment, a fine opaque red pigment and some black are present. The preparatory layers and painting technique of the painting *Portrait of a Lady*, attributed to Rogier van der Weyden, were described by Metzger *et al.* (1998). Two distinct intermediate layers were applied over the calcium carbonate ground. The main inorganic components, identified by SEM-EDX, were earth pigment, lead white, calcium carbonate, bone black and carbon black. No identification of the medium is reported.

The infrared reflectography study of the underdrawing in the paintings attributed to Rogier van der Weyden and his workshop, suggests that a black paint was applied with a brush, leaving a solid line also visible when observed in cross-section. The study of different paintings suggests the use of a paint of identical working properties but possibly different composition (Campbell *et al.*, 1997a). The scarce and incomplete information reported on binding media of *imprimatura*, preparatory or intermediate layers reflects the difficulty associated with the analysis of such layers. In this paper the detailed chemical description of the composition of the preparatory layers, in cross section, is given by a combination of analytical microscopic techniques.

Experimental section

Light Microscopy

The light microscopy images were obtained on a Leica DMR microscope. Normal light was provided by a halogen projection lamp and ultraviolet light by an OSRAM HBO 50W/L2 short arc mercury lamp. Images were recorded with a Nikon digital still camera DXM1200.

Secondary ion mass spectrometry (SIMS)

Static SIMS

The static SIMS was performed in Physical Electronics Trift II TOF SIMS. The pulse beam was non-bunched with a pulse width of 20 ns and a spot size of 120 nm. The surface of the sample was scanned with a 15 keV primary ion beam from an $^{115}\text{In}^+$ liquid metal gun. The primary beam was rastered over a $50 \times 50 \mu\text{m}$ area divide in 256×256 pixels. All measurements were charge compensated with electron pulsed between the primary ion beam pulses.

Nano SIMS

Dynamic nano-SIMS measurements were performed in CAMECA nanoSIMS 50. The CAMECA NanoSIMS 50 is an ion microprobe based on a double focusing mass spectrometer that allows parallel collection of five masses (or seven with the NS50L). The coaxial objective and extraction lens permit a very short working distance. This ensures low aberration coefficients for a high lateral resolution, and a quasi-full collection of the secondary ions, requisite for high transmission. All measurements are done at a high mass resolution (without any slit or aperture in the spectrometer, $M/dM = 2500$).

Designed to work in dynamic SIMS mode (optimization of the element/isotope secondary ionization yield by the implantation of reactive primary species simultaneously with the sputtering process), the NanoSIMS 50 is equipped with two reactive ion sources. The analysis was performed with 16 keV Cs^+ primary ion, detecting negative secondary ions (resolution 50nm) or 16keV O^- primary ion detecting positive secondary ions (resolution 200nm). Mass Resolution M/dM was 2500 except for Fe measurements ($\text{MRP} = 4500$ to remove CaO mass interference). The sample surface was gold coated (30 nm). This was sufficient to avoid any charging so no electron charge compensation was needed. The area for nanoSIMS analysis

was sputtered with a high intensity beam to remove the gold and expose the surface for analysis.

Scanning Electron Microscopy

Scanning electron microscopy in association with energy dispersive X-ray analyses were performed on a XL30 SFEG high vacuum electron microscope equipped with a EDX system. EDX analyses were performed at a spot size of 4 and an acceleration voltage of 10 kV. EDX mapping parameters were area resolution 256 x 200, 1024 frames, 200 ms dwell time, 50 ms amplitude time. The sample was carbon coated to improve surface conductivity. Back scattered electron images describing of the whole underdrawing and preparatory layer have been shown elsewhere (Boon *et al.*, 2005).

Samples

Sample taken from Brinkman's reconstruction panels

Samples from the Brinkman reconstruction panels were studied with chemical microscopy. The media tested for the isolation layer included stand oil, leaded oil (linseed oil boiled with PbO), leaded oil with 1/3 glue emulsion and raw linseed oil with 1/3 glue emulsion (Brinkman, 1993; Brinkman, personal communication 2005). The sample boards were prepared in 1979 and have been kept under ambient conditions since then.

Paint sample A166/1b

Paint sample (A166/1b), supplied by van Asperen de Boer, was taken from the virgin's blue robe in a crack between two planks of the 15th century panel painting *The Descent from the Cross* attributed to Rogier van der Weyden (Prado, Madrid).

In all cases the samples were embedded in Technovit 2000LC resin, and dry polished with micromesh cloths (final step 12 000 mesh).

Analytical results

The characterisation of the preparatory layers was done by the combination of different analytical microscopic techniques. These results were partially presented elsewhere (Ferreira *et al.*, 2005)

Brinkman Reconstructions

The analytical study was performed with the aid of light microscopy equipped with visible and ultraviolet light sources, imaging FTIR (Fourier transform infrared spectroscopy) and SEM-EDX. The results show that in all cases there is a degree of penetration of the medium from the isolation layer in the porous ground layer. When raw linseed oil and glue emulsion are used in the isolation layer, no distinct separated layer can be seen above the ground suggesting that it is entirely absorbed by the porous chalk/ glue ground layer. In contrast, when the isolation layer consists of stand oil, leaded oil or leaded oil and glue emulsion a distinct layer is detected above the ground although partial absorption in the ground is indicated by the analytical results.

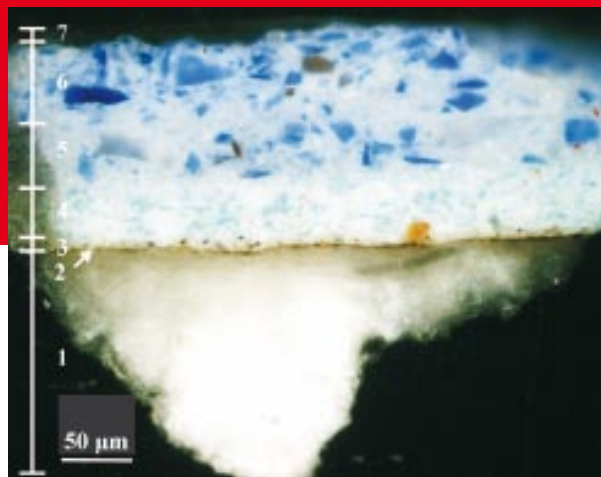


Fig. 1. Light microscopic image of the cross section of a sample from the blue robe of the Virgin Mary in *The Descent from the Cross* by Rogier van der Weyden.

The leaded oil isolation layer is rich in lead carboxylates or soaps resulting from the reaction of the oil and the lead oxide during the last 25 years. This is clearly detected by FTIR. Also the lead dispersed throughout the medium is clearly visible in the isolation layer by SEM-EDX and interestingly is distributed in a heterogeneous way, the top area of the isolation layer being richer in lead compared to the lower part. When the leaded oil is mixed with glue the concentration of lead carboxylates is lower and its detection by FTIR proves difficult. The relative concentration of lead in the emulsion is also very low in the SEM-EDX mapping data. This is a particularly important finding because it means that leaded oil addition by painters may be obscured or an absence of lead in an isolation layer can be misinterpreted.

Paint sample A166/1b

Light Microscopy

The light microscopic description of the cross-section under investigation was given in the Introduction (Fig. 1).

Scanning Electron Microscopy/Energy dispersive X-Ray microanalysis.

The main element detected in the ground is calcium confirming the FTIR suggestion of calcium carbonate ground.

The reliable analysis of the extremely thin, highly organic layers 2 and 3 required a different approach than that used for the characterisation of the blue paint layers (Keune *et al.*, 2004). SEM/EDX was performed at higher magnification (> 3000x) in these layers using low acceleration voltage (BSE mode 10 kV), to limit the depth of the electron penetration. Thus, the elemental information is obtained from a smaller sample volume, improving accuracy in elemental distribution at and near the surface. This approach assisted in establishing the distinct properties of this layer.

The element distribution maps (Fig. 2) show that the underdrawing layer is mainly characterised by a higher intensity of carbon. The isolation or intermediate layer is characterised by the higher concentration of carbon (Fig. 2c) in comparison to the

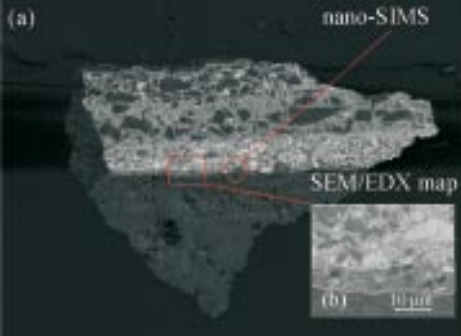
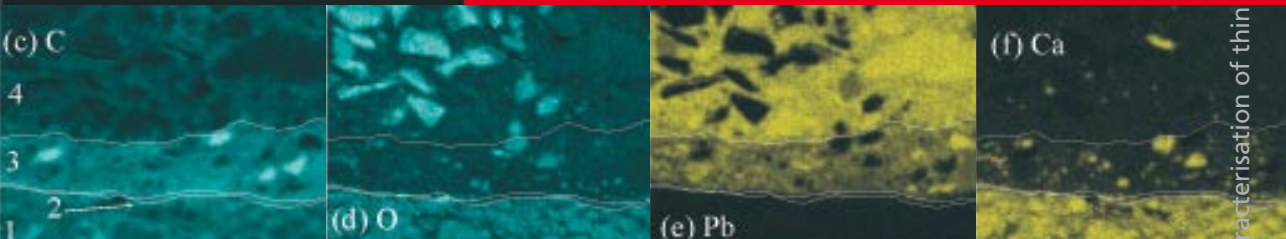


Fig. 2. Backscattered electron image (a) of the cross section of the blue paint sample from the robe of the Virgin Mary in the *The Descent from the Cross* by Rogier van der Weyden. The indicated area was measured for the 1) X-ray maps and 2) Nano-SIMS. Detailed backscattered electron image (b) of the preparatory layers. c-f) X-ray maps of carbon (c), oxygen (d), lead (e) and calcium (f).



medium. Discrete hot spots of carbon associated with the black particles described by light microscopy (possibly carbon black pigments particles) are found. Calcium containing particles are also found dispersed in the layer (Fig. 2f). The lead map (Fig. 2e) is very elucidating about the properties of this layer. Few high density areas can be seen in the BSE images indicating only a few lead white particles are dispersed in the layer. These particles are indeed matched by the hot spots on the lead map of layer 3. However the lead map shows that lead is also finely dispersed in the layer and not only associated with the lead white particles. The suggestion of lead being present in lead carboxylate is coherent with the finely dispersed lead present throughout the layer. The few discrete orange particles described by light microscopy are iron and oxygen containing and possibly iron oxide particles. In summary the SEM/EDX analysis of layer 3 shows that this layer is medium rich (carbon SEM map more intense in this layer), that the lead is present in much smaller particle sizes as well as finely dispersed through the layer matrix. The layer also contains a small amount of iron oxide and calcium carbonate (chalk).

Secondary ion mass spectrometry (SIMS).

Static SIMS

Little evidence of fatty acids was found in layers 1-3 in the previous study (Keune *et al.* 2004). It was postulated then that the medium could be a proteinaceous one. However it was also observed that the fatty acid yields are much higher when associated with high density lead white particles present in much lower concentrations in the preparatory layers and therefore a more detailed analysis of the layers 1-3 was required.

The negative ion SIMS spectrum of the combined layers 2 and 3 shows clearly the presence of peaks characteristic of oil binding medium although in low yields. The peaks corresponding to the deprotonated palmitic (m/z 255) and stearic acid (m/z 283) are clearly present as well as the fragment ions of fatty acyl chains (m/z 99, 113, 127, 141) and those corresponding to the short chain fatty acids octanoic acid

(m/z 143), nonanoic acid (m/z 157) and decanoic acid (m/z 171). A study of multi-layered paint systems with pure protein layers (Ferreira *et al.*, 2005) has suggested that, in negative ion mode, the peaks corresponding to peptide bond fragments (m/z 26 CN^- , m/z 42 CNO^-) can be indicative of these protein containing layers. However these studies were only conducted on freshly prepared samples and little is known about the SIMS ionisation behaviour of proteins in pigmented and/or aged samples, which suggests that further work is required in this area. Having said that, no peaks indicative of the presence of proteins were found (the counts were very low and detected in all the area analysed), suggesting that the medium is simply a drying oil and not an emulsion.

The positive ion SIMS spectrum shows the presence of lead and calcium in the intermediate layer.

Nano SIMS

With the purpose of further clarifying the nature of the medium in the layer 3, nano-SIMS was performed. The mass information obtained by this technique is different from that obtained by static SIMS. The ion dosage and energy in each analysed spot is higher and only small fragments and elements can be detected by this method. The nano-SIMS ^{12}C ion image (Fig. 3a) confirms the high carbon content of layer 3. The advantage of nano-SIMS is the high sensitivity to the detection of ^{14}N detected as the $^{12}C^{14}N$ fragment when both ^{14}N and ^{12}C are present in the analysed spots. The $^{12}C^{14}N$ image (Fig. 3c) indicates that ^{14}N is mainly present in the ground layer 1, suggesting this to be a glue containing ground, in keeping with the known 15th century tradition of panel painting preparation. Very low intensities of the $^{12}C^{14}N$ fragments were detected in layer 3 suggesting little or no protein is present in layer 3.

The ^{16}O image (Fig. 3b) seems to suggest that this ion is present in higher intensities in association with the azurite and lead white pigment particles but can be detected throughout the area analysed and therefore is also present in the medium.

The ^{35}Cl ion is detected mainly in the lower region of the azurite layer and associated with the lead white particles in layer 3. The presence of chloride in association with lead white has been described previously however the higher concentration of a particular region in a layer is a new observation. At this point in time we have no hypothesis to explain this observation.

The nano-SIMS analysis has shown that the binding medium of the isolation layer does not seem to contain any proteinaceous material.

Discussion and conclusions

The example given shows the strength of the combined information obtained from the different imaging techniques in the characterisation of cross-sections of multi-layered paint samples.

The information obtained from the spatially resolved analytical techniques identifies the inorganic components, namely pigments and driers, in the layer of interest, *i.e.* the thin intermediate layer 3. Significant information on the organic fraction, in the present example the binding medium, can also be provided by these techniques. Organic rich layers can be visualised by SEM/EDX and nano-SIMS. More specifically,

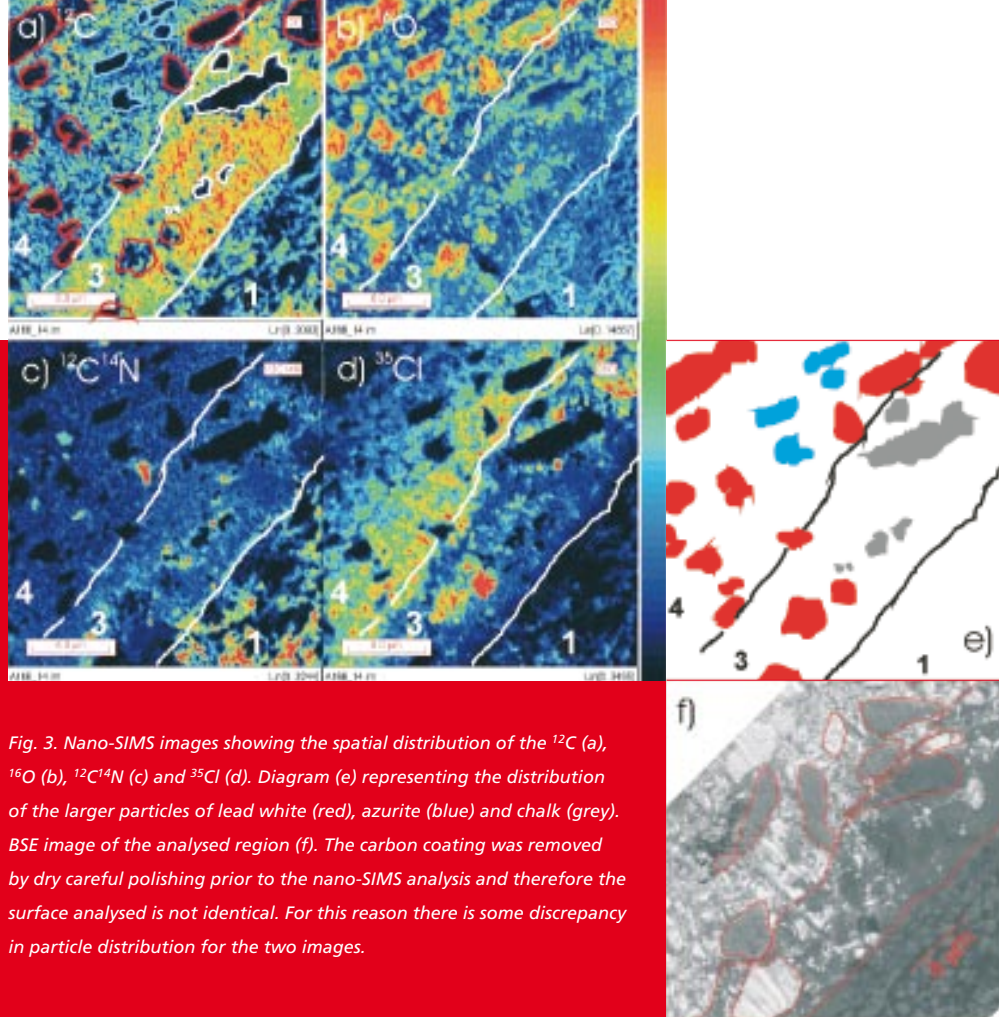


Fig. 3. Nano-SIMS images showing the spatial distribution of the ^{12}C (a), ^{16}O (b), $^{12}\text{C}^{14}\text{N}$ (c) and ^{35}Cl (d). Diagram (e) representing the distribution of the larger particles of lead white (red), azurite (blue) and chalk (grey). BSE image of the analysed region (f). The carbon coating was removed by dry careful polishing prior to the nano-SIMS analysis and therefore the surface analysed is not identical. For this reason there is some discrepancy in particle distribution for the two images.

oleaginous binding medium is identified with static-SIMS by the detection of fatty acids.

In the paint sample A166/1b nano-SIMS suggests the presence of nitrogen containing medium in the ground layer but not in layer 3.

The SEM/EDX shows that a high concentration of carbon in the brown underdrawing layer. This information combined with the light microscopic observation leads to the conclusion that the underdrawing was a carbon black applied in a fluid medium. This is supported by interpretation of van Asperen de Boer *et al.* (1992) based on infrared reflectographic data. The detailed analysis of the isolation or intermediate layer shows that it has the chemical characteristics of a leaded oil with gel properties. Lead white particles are also found in the layer but the lead SEM/EDX map shows that lead is dispersed throughout the layer and not necessarily associated only with the pigment particles. Chalk, carbon black and iron oxide particles are also detected in this layer. High magnification SIMS shows no evidence of the presence of proteins in the intermediate layer, reinforcing the static SIMS indication for the presence of an oleaginous medium.

To conclude, our observations on the characteristics of the binding medium of the

intermediate layer (layer 3) support the observations of Brinkman (1993) building on the earlier work of the Coremans team (1953). It appears that van der Weyden employed a lead treated oil based medium in an isolation layer above his underdrawing.

Acknowledgements

The authors would like to thank CAMECA (Courbevoie, France) in particular François Hillion and François Horr ard for the use of the Nano-SIMS and the processing of the data. Prof. J.R.J. van Asperen de Boer is thanked for providing the sample of *The Descent from the Cross* by Rogier van der Weyden for cross-section preparation and analysis. The research at AMOLF is embedded in the FOM research programme nr. 49 "Mass spectrometric imaging and structural analysis of biomacromolecules". This work is part of the 'De Mayerne' programme funded by the Netherlands Organisation for Scientific Research (NWO) and the Foundation for Fundamental Research on Matter (FOM), a subsidiary of the Netherlands Organisation for Scientific Research (NWO).

References

- Boon J.J., Ferreira E.S.B., Keune K. (2005). *Imaging analytical studies of Old Master paints using FTIR, SIMS and SEMEDX of embedded paint cross-sections. Microscopy and Micro-analysis*, 11, pp 1370-1371.
- Kirby J., Roy A., Spring M. (2002). *Materials of underdrawing In: Art in the Making: Underdrawing in Renaissance paintings Bromford D. (Ed), National Gallery, London, pp 26-37.*
- Ferreira E.S.B., Keune K., Boon J.J. (2005). *Combined Microscopic Analytical Techniques as Diagnostic Tools in the Study of Paint Cross-Sections: Case study of a sample from a 15th century painting, The Descent from the Cross by Rogier van der Weyden. 4th biennial meeting of the IPCR (Instituto Portugu es de Conserva o e Restauro), Lisbon, Portugal, 24-25 November 2005.*
- Brinkman P., Kockaert L., Maes L., Masschelein-Kleiner L., Robaszynski F., Thielen E. (1984). *Het Lam Gods retabel van van Eyck. Een heronderzoek naar de materialen en schildermethoden. 1. De plamuur, de isolatielaag, de betekening en de grondtonen. Bulletin IRPA-KIK* 20, pp 137-166.
- Brinkman P. (1993). *Het geheim van van Eyck: aantekeningen bij de uitvinding van het olieverven. Waanders, Zwolle.*
- Campbell L., Foister S., Roy A., (1997). *The methods and materials of Northern European painting 1400-1550. National Gallery Bulletin, vol 18, pp 6-55.*
- Campbell L., Foister S., Roy A. (1997a). *The materials and technique of five paintings by Rogier van der Weyden and his workshop. National Gallery Bulletin, vol 18, pp 68-86.*
- Coremans P. (1953). *L'Agneau mystique au laboratoire. Antwerpen, 76*
- Keune K., Boon J.J. (2004). *Imaging Secondary Ion Mass Spectrometry of a Paint Cross Section Taken from an Early Netherlandish Painting by Rogier van der Weyden. Analytical Chemistry, 76, pp 1374-1385.*
- Metzger C.A., Palmer M. (1998). *The Washington Portrait of a Lady by Rogier van der Weyden Reconsidered in Light of Recent Investigations. In: Painting Techniques, History, Materials and Studio Practice, IIC congress, Dublin, 7-11 September 1998, p. 94-97.*
- van Asperen de Boer J.R.J., Dijkstra J., van Schoute R. (1992). *Underdrawings in Paintings of Rogier van der Weyden and Master of Fl emalle Groups. Nederlands Kunsthistorisch jaarboek 1990, volume 41.*

Historically Accurate Reconstructions of Oil Painters' Materials: An overview of the Hart Project 2002-2005

HISTORICALLY ACCURATE RECONSTRUCTIONS TECHNIQUES (HART)

Abstract

This paper describes a project to explore artists' past oil painting techniques and materials using reconstructions prepared with as much historical accuracy as possible. Extensive research is undertaken to identify documentary sources covering technical information contemporary with the period being investigated, and to find materials now that can represent what would have been used in the past. While this work relies on chemical analyses from actual historic paintings, at the same time it contributes to future analyses by providing reference material for analytical standards. Reconstructions of multilayer paint/ground composites offer visual comparisons with paint/ground samples from actual paintings. The preparation of paint and grounds in itself provides important information on workshop practice and artists' experiences with the limitations and strengths of individual materials.

¹ Tate Britain, Millbank, London, SW1P 4RG, England, leslie.carlyle@tate.org.uk

Introduction

The investigation of artists' oil painting materials and techniques has traditionally been undertaken through scientific analysis of tiny paint samples, sometimes supplemented with an investigation of artists' accounts and recipes contemporary to the work of art. The importance of documentary sources in providing insight on chemical findings has long been recognized, and is currently being furthered through ATSR (Art Technological Source Research group) (Stijnman 2005). A relatively late-comer to these investigative techniques, is the concept of re-creating old recipes with as much historical accuracy as possible in order to understand more about the artist's first-hand experience with his materials, what governed his choices and the final appearance of his work (Carlyle *et al.* 2004).

The HART project (Historically Accurate Reconstructions Techniques) was designed to provide reconstructions of grounds, paint and paint composites for specific projects in the De Mayerne Programme. Paint reconstructions with traditionally prepared lead white pigment helped to elucidate the relationship between lead white pigment and oil (its chemistry, rheology, covering and hiding power, as well as its colour, and transparency). These factors were important to various De Mayerne Projects such as "The Coordination Chemistry of Lead and Chemical Changes in Ageing Oil Paintings"; the "Imaging Microscopy of Paint Cross-Sections," the investigation into lead soap aggregates, and the study of darkening and transparency in 19th century paintings (Yoshiko Shimadzu's PhD project; ICN/AMOLF). Paint and ground reconstructions were prepared to aide in the interpretation of Van Gogh's painting technique ("The Painting Materials and Technique of Vincent Van Gogh"), and finally paint composites (layers of ground and paint with intermediate layers in between) were prepared to provide reference material for microscopic investigations of paint samples and for the work carried out by Katrien Keune for her PhD relating to the De Mayerne project "Imaging Microscopy of Paint Cross-Sections."

HART project reconstructions of oil paints, grounds and paint composites are available to future researchers. This unique set of well characterised material can be mined to answer a wide range of questions, some of which are yet to be asked. It is anticipated that these samples will prove a valuable resource well into the future. Sets of samples are housed at ICN, the Van Gogh Museum and the Tate U.K.

Historical Recipes Database

Reconstructions of historic artists' materials cannot proceed without reference to contemporary documentary sources. This information is essential for insight into what materials were used and in what way. Historical recipes for the preparation of artists' materials provide a rich source of information for modern researchers on the methods and materials used by artists in the past. In the earliest sources, the instructions tend to be fragmentary, but by the second half of the 18th century, and throughout the 19th century, they are frequently quite comprehensive in scope. By comparing a large collection of instructions for the preparation of pigments, drying oils, mediums, and

varnishes over the centuries, it is possible to identify representative recipes, and to track the introduction of new materials. A close reading of the more recent recipes can often assist in interpreting incomplete instructions in the earliest sources. Familiarity with the materials listed in published sources then leads to the successful interpretation of hand written accounts where synonymous or truncated terms are used.

A significant part of the HART Project was to gather, transcribe and index historical recipes from the 16th to 19th centuries in western European manuscripts and published sources. This is detailed in (Carlyle *et al.* 2005). The database was initially intended as a research tool for the HART Project, but it is anticipated that this resource will be made available to other researchers.¹

Reconstructions

The next step, to recreate historical recipes, not only results in a better understanding of the original instructions, but often new and unexpected information is gained through this process. For example, some might have thought that the flow properties (rheology) of a simple mixture of pigment and oil is more or less fixed, and that adjustments in texture and flow were primarily achieved through the addition of paint mediums. In the past three hundred years arguments have raged on whether or not the old masters added resins to their oil paint to alter its behaviour during application.² Based on recent analyses and a knowledge of more recent practices in the 19th century, other materials have also been considered as possible additions to 17th century oil paint, including aqueous based materials such as whole egg (van der Wetering 1997), or animal or vegetable gums³ (Groen 1997; Middelkoop 1998; Noble 1999).

¹ As part of her PhD research with the University of Amsterdam, the HART Research Associate, Maartje Witlox will refine and complete the database. It primarily covers recipes on artists' grounds, but necessarily includes information on the raw materials used in these grounds such as recipes on oil processing, lead white manufacture and size preparations.

² "Most ancient painters of the Venetian and Flemish Schools did not paint, as we do, with pure oils, but...they tempered their colours also with varnish, and to this is to be attributed the great preservation of their pictures." [p. xxiv in Mérimée, J.F.L., (1839). *The Art of Painting in Oil, and in Fresco: Being a History of the Various Processes and Materials Employed, from its Discovery, by Hubert and John Van Eyck, To the Present Time....* London. [Originally published in French in 1830.]. Certainly small additions of pine resin were added to the binding media of certain pigments, for instance copper greens. GCMS analysis of a scraping from a green glaze in the background of a painting by Pieter Pietersz. (MH inv. no. 914) indicated an oil/resin binding medium (FOM, 1999). From Noble, P., Pieter Pietersz. *Portrait of a man*, Technical description, 1997, modified 1999, Mauritshuis Conservation Studio. Small additions of pine resin have also been found in red glazed passages and brownish glazes in paintings by Van Dyck. See Raymond White "Van Dyck's Paint Medium" *National Gallery Technical Bulletin*, Vol.20, (1999), p.84-88.

³ FTIR spectra indicated the presence of a gum in the oil binding media of thickly applied organic red mixtures, in Rembrandt's *The Anatomy Lesson of Dr Nicolaes Tulp*, MH inv.no.146 (ICN, 1998) and *Head of a man in a plumed hat*, MH inv.no.149 (ICN, 1999).

Reconstructions of popular 19th century mediums have been studied in some detail (Townsend *et al.* 1998; Kokkori *et al.* 1998), and empirical trials have been carried out with the addition of other materials during paint-making workshops.⁴ The profound influence of these materials on oil paint strengthened the view that rheology is altered primarily through additions. However work carried out in a MOLART Fellowship (Carlyle 2001a) challenged this assumption and offers a new perspective. The MOLART fellowship (Carlyle 2001b), an investigation of various historical recipes for processing linseed oil which relied on freshly expressed oil from a single seed lot, was primarily intended to study film formation defects in hand-ground paint prepared with these oils, and to provide a reference set of traditionally prepared oils for research on the chemistry of drying oils within the MOLART Programme (van den Berg *et al.* 2004; Vermist 2000; Van den Berg 2002). An unintended result was the discovery that the rheology of lead white oil paint is highly dependent on the method of oil processing. Clear differences in the handling properties of lead white paint could be distinguished according to the lead compound used to treat the oil prior to use (eg. litharge (lead (II) oxide), lead acetate and lead subacetate), and the degree of heat applied to the oil (this latter observation was also made by Hayo de Boer (ICN) in previous studies on Rembrandt's paint) (Groen 1997).

This approach, that the oil processing alone can play a role in the handling properties of the paint was explored further in the HART Paint Project, where attempts to recreate the flow-properties of Van Gogh's paint were based largely on investigating the relationship between linseed oil processing and the addition of poppy oil.

Reconstructions as reference material

Reconstructions of old recipes are not only valuable for the new information gained during preparation, they provide scientists with representative samples essential to their work. The study of artists' oil painting materials from historic and modern works relies heavily on analyses from paint cross-sections. Identifying individual components in samples of initially unknown composition can be problematic: some materials are difficult to find when they appear in a mixture, and unprocessed materials used as "standards" for analysis are not always accurate reflections of the same materials after processing. For example, documentary evidence indicates that Whistler used copal oil varnish in his oil paint, but it was not detected with DTMS (Towsend 1994). Problems with identifying this substance were highlighted when reconstructions of copal-oil varnish prepared at the Canadian Conservation Institute (Carlyle *et al.* 1994; Carlyle *et al.* 1999) were analysed with FTIR and copal resin was not detected.⁵ One of

⁴ Hand-grinding of traditional oil paint with the addition of egg and various other additives (megilps, copal varnish, starch, etc.) has been the subject of workshops for conservators, art historians, and students worldwide. These workshops have been conducted by Dr. Carlyle and by Sarah Cove, who specialises in the 19th-century British painter John Constable.

⁵ Analysis was carried out by Scott Williams, Conservation Processes and Materials Research Division, Canadian Conservation Institute, 1030 Innes Road, Ottawa ON K1A 0M5.

the outcomes of the MOLART Programme was the development of an analytical method which will detect this material, and which takes into account the extreme heat processing that fossil resins undergo during varnish manufacture (Van den Berg *et al.* 1999).

Relevance to other projects within the De Mayerne Programme

The preparation of reconstructions, although an end in itself, was also directed towards answering specific questions posed within the De Mayerne Programme. For example what role does the chemical formula and morphology of lead white pigment play in the properties of oil paint made with this pigment? What are the mechanisms responsible for the development of the paint defect characterised by the formation of lead soap aggregates? What ingredients or factors contribute to the texture and appearance of Van Gogh's paint, did he add modifiers himself, or was the commercial colourman responsible for the paint consistency we see on his paintings? What role did ground preparations in his works play in the way his paint handled and now appears?

The importance of historically accurate materials

When reconstructions are intended for molecular investigations of artists' varnishes, oils, mediums and pigments, it is imperative that they are prepared with historically accurate materials. Varnishes prepared with the now popular dammar resin, cannot represent 18th century varnishes, since dammar does not appear to have been introduced into the artists' market before 1827 (Lucanus 1829). Modern, commercially prepared drying oils available from the leading colourmen, are not refined and processed according to traditional methods. Therefore reconstructions made with these commercially available oils are not representative of what was used in the past. Furthermore, the lack of information on seed lots and processing methods makes it impossible to compare the exact chemistry of one set of paint samples made with a commercial oil with another made at a different time and with a different batch of commercial oil. Mixing additives or mediums to modern tube paints in order to evaluate their effect on oil paint is equally problematic since modern tube paints no longer contain ingredients consistent with paints produced in the past. Linseed and poppy oils are replaced by safflower oil, lecithin is added to wet-out pigments during grinding, the pigments themselves are micronised (ground extremely finely), and some are even coated with phthalates or silica to enhance their suitability in modern paint systems.

Even so-called traditional materials cannot be taken at face value. Rabbit-skin glue, the mainstay of canvas sizing, is now prepared from generic animal skins (likely cattle) (Young – Courtauld, personal communication).

Modern tubes of lead white oil paint contain precipitated lead white pigment and sometimes, a significant proportion of zinc white. Lead white prepared according to the Dutch stack process, the method used exclusively until the eighteenth and nineteenth centuries, is no longer made.

Throughout the HART Project, every effort was made to identify what materials would have been in use at a given time, and to source materials that would be appropriate.

Documentation of Historically Accurate Oil Paint Materials Reconstructions

For the Hart Project reconstructions to be valuable to future researchers it was essential to document all materials sourced and to retain samples of the raw materials. Each recipe that was followed required detailed recording of information: not only on the materials used (e.g. date and conditions of oil pressing, seed lot, etc.) but on their preparation and application. This information is available in the "HART Report 2002-2005", which consists of over 400 pages of data (sample lists, codes used, tables of ingredients etc.) including observations on the behaviour of materials in preparation, during application and immediately after, as well as 25 Powerpoint presentations which illustrate sample preparation and initial appearance. A copy of the report is available with each sample set (at ICN, Van Gogh Museum and Tate). Copies were also deposited at the Canadian Conservation Institute (CCI) and at FOM-AMOLF.

Another consideration for the future value of this work is storage conditions. For example, samples must not be stacked (although appearing dry, oil paint can easily remain sticky), adequate air circulation is needed, and surrounding storage materials must be relatively inert (e.g. not contributing plasticizers, or off-gassing and thereby contaminating the samples).

OVERVIEW OF INDIVIDUAL HART PROJECTS:

The Lead White Pigment Project

The role of lead white pigment formulations in paint rheology

Late nineteenth century and early twentieth century oil paint and lead white pigment manufacturers reported that variables in lead white pigment chemistry as a result of manufacture and storage led to differences in handling qualities, covering power and hiding power in lead white oil paints (Lambert 1902; Cruickshank 1924; Stewart 1950). The proportion of "lead hydroxide" present was seen to be particularly important (Carlyle 2001a).

Two different lead white pigments were used to produce hand-ground oil paint during the MOLART Fellowship: one, thought to be made by the old Dutch stack process from a now defunct supplier, and another, assumed to be a modern precipitated lead white, from a supplier that is still active (Kremer-Pigmente). During grinding, differences in oil absorption, handling characteristics (rheology), and colour were observed. Yet judging from their morphology (investigations were made using scanning electron microscopy), both lead whites were of distinctly modern manufacture.

A lead white produced by the traditional stack method was made available for HART project reconstructions. This lead white is distinctly different from both modern varieties in its particle size and shape, and takes half the amount of oil to produce the same consistency of paint.

The development of transparency in lead white paints

The gradual development of transparency in lead white oil paint has long been recognized (Carlyle 2001a; Townsend 1993). This poorly understood phenomenon profoundly influences the interpretation of images from paintings as early as the 16th century through to the 19th century. Passages containing once opaque lead white, now reveal underdrawing and preparatory layers originally meant to be hidden by subsequent layers of paint. Documentary sources report that changes in transparency can occur within the first few years after the paint is applied (Muckey 1882). Yet not all lead white passages are subject to this defect.

Some nineteenth century documentary sources identified the “lead hydroxide” content in lead white formulations as a major contributor to a lack of opacity in fresh oil paint (Carlyle 2001a), and one early twentieth century source describes a chemical interaction with lead hydroxide and the oil which leads to transparency (Hurst 1906). Many early sources report that the exact chemical formulation of lead white can be highly variable (Hurst 1906). Twentieth century literature reveals that there are at least two different forms of basic lead carbonate hydroxide associated with lead white pigments: hydrocerussite, $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ and the more basic plumbonacrite, $6\text{PbCO}_3 \cdot 3\text{Pb}(\text{OH})_2 \cdot \text{PbO}$, which is the first to form on metallic lead in the presence of acetic acid vapours (produced during the traditional Dutch stack process of lead white pigment manufacture) (Stewart 1950; Olby 1966; Shoosmith *et al.* 1988; Thickett 1997; Tétrault *et al.* 1998). During the De Mayerne Programme, an investigation of different lead white pigment sources was carried out in an attempt to understand the relationship of the chemical formula to the manufacturing process and whether this can change in the oil paint environment.

Reconstructions of traditionally prepared stack process lead white paint were made with two commonly used extenders (chalk (calcium carbonate) and barium sulphate) in a series of stepped proportions (e.g. 1:2, 1:1, 1:3 etc) to investigate the transparency of these materials in oil, and to determine the accuracy of SEM-EDX quantification software with cross sections from historical paintings (Haswell 2006). Although resources were not available within the HART Project to study the transparency phenomenon in detail, the samples now prepared can form the basis of future work in this area.

Lead soap aggregates

Some historic lead white paints exhibit small regularly shaped translucent protrusions which disrupt surface texture and disturb the continuity of the paint surface. Protrusions caused by the aggregation of lead soaps found in a number of 17th century paintings have been the subject of intense investigation in the Mauritshuis and at FOM-AMOLF (Boon *et al.* 2002; van der Weerd *et al.* 2002; Noble *et al.* 2000). Similar protrusions were also identified on 19th century paintings (Carlyle 1999; CCI 1992). An important component of the HART Lead white project was to explore mechanisms which might lead to the formation of this particular paint defect.

The Van Gogh Ground Project

The HART Ground Project grew out of the investigation of the handling properties of Van Gogh's paint. It was designed in collaboration with Ella Hendriks, principal coordinating investigator for the De Mayerne Project "The Painting Materials and Technique of Vincent Van Gogh." In order to evaluate how Van Gogh's oil paint behaved, it was felt that grounds typical of the variety he used should form the substrate. A group of 6 paintings from Van Gogh's oeuvre were chosen to represent the range of grounds he used. Historical recipes for sizing and ground preparations were studied along with 19th century information on grounds and their ingredients kindly made available through the British colourman Winsor and Newton (see below). Extensive analytical work had been carried out on Van Gogh's grounds at ICN and in collaboration with Shell International Chemicals B.V., Amsterdam. This work gave the HART project a valuable overview of the ingredients found in his grounds.

The Paint Project

The flow properties of oil paint

Painters in the past have exploited a wide range of textures from highly impasted paint, such as we see in Van Gogh and in the highlights of Rembrandt, to the smooth, enamel-like surfaces found in the works of the Fijnschilders, such as Dou or Van Mieris. How painters achieved such variety in texture is not fully understood. Although analysis can provide a list of materials present, only by reconstructing oil paints using historically accurate ingredients, can the proportions of materials and their individual functions be appreciated.

In the De Mayerne Project, "The Painting Materials and Technique of Vincent Van Gogh," it was recognized that an understanding of the appearance and condition of Van Gogh's paintings hinges on knowing what pigments, binders, driers, stabilizers and extenders have been used in his commercially prepared paint. Whether or not Van Gogh manipulated the texture of his paint by adding other materials can then be determined.

Artist Colourmen and Colourmen archives

Very little is known about the composition of 19th century commercially prepared oil paints. Until the HART Project, only one colourman's archive was available for study (the British colourman, Roberson, with records dating from 1828 to the end of the century) (Carlyle 2001a; Woodcock 1995). Unfortunately very few recipes for oil paint are included in this resource. The HART Project was very privileged in being allowed access to the private archive of the British colourman, Winsor and Newton, who began operations in the 1830s and continues today as a world leader in artists' supplies. HART staffmembers were the first outside researchers to be allowed access to Winsor and Newton's recipe books in the 170 year history of the company. The outcome was a project to create an innovative database to make a selection of this archive accessible. In 2004 this became another De Mayerne Project funded by NWO (see paper, Clarke and Carlyle in this publication).

The HART project also benefited from generous cooperation from other colourmen

who opened their doors to the project and provided assistance and equipment. Old Holland Classic Oil Paints (Driebergen-Holland) made their extensive pigment collection archive available and spent many hours machine grinding oil paint for the HART Project with HART project ingredients. Royal Talens was also generous with their time by carrying out rheology measurements on HART paint samples. In the early days of the project, Michael Harding (Michael Harding's Artists Oil Colours), provided a tour of his facility and insight into commercial paint manufacture. HART reconstructions of oil paint were based on information gained through analyses, documentary evidence and the assistance of these colourmen. This work is detailed in the "HART Report 2002-2005".

Reconstructing paint composites

Historic documentary sources describe methods of oil painting in a series of discrete layers. Following the layer structure described in these sources would lead to the layer structure listed in box 1 (ordered from the top surface of a painting to the bottom):

Varnish layer	(or layers)
Finishing layers	(glazes, scumbles based on oil)
The last painting	(final layer of oil paint)
Second painting	(second layer of oil paint)
Intermediate layer	(oil or varnish)
Deadcolouring	(first layer of oil paint –can be aqueous binder e.g.protein)
Sealing layer	(or isolation layer: oil or varnish)
Underdrawing	(with dry material or liquid)
Toning layer	(or imprimatura, coloured layer on top of ground)
Sealing layer	(or Isolation layer: oil or varnish)
Ground	(one or more applications)
Size	(glue based (protein) or starch)
Canvas	

Cross sections from paintings from different schools of painting across the centuries all contain at least some of these layers. Intermediate layers consisting of resin or oil and protein-rich layers are not clearly visible under normal light microscopy. As a result, although documentary evidence for their use by artists exists (Carlyle 1999), researchers failed to appreciate their importance in painting techniques until ultra violet (UV) light microscopy became a common tool for examining cross sections in the 1980s. Under UV light layers rich in resins, oil and proteinaceous materials fluoresce and are now routinely seen in cross sections.

In the HART project a set of layered composites prepared with historically accurate materials and techniques was made to verify the appearance of specific intermediate layers consisting of oil, resins and proteinaceous materials.

Until the Hart project, the general assumption has been that thin layers of fluorescing



Fig. 1. Cross-section of ground reconstruction in ultraviolet light (200x magnification). Bottom layer is chalk (calcite) with an oil binder (1:1 mixture of raw linseed oil and litharge treated drying oil), top layer is stack method lead white with 7% by weight barium sulphate (no processing agents added). The layer in the centre is fluorescing and appears to be an oil layer. On an unknown sample, this could be interpreted as a deliberate addition of a thin layer of oil between ground layers.

materials visible in cross-sections from actual paintings represent deliberately applied intermediate layers. However, in one particular reconstruction such a layer of oil found between layers in a ground was not deliberately applied, rather, it occurred as a natural consequence of the oil binder separating from a chalk/oil ground (see Figures 1 and 2 and note 6).

Another finding regarding intermediate layers, resulted from a HART project reconstruction studied by Katrien Keune for her PhD, "Imaging Microscopy of Paint Cross-Sections" (part of the De Mayerne Programme). A layer of mastic resin varnish had been applied as an intermediate layer over dried paint made with linseed oil binder. A paint made with a poppy oil binder was then applied on top of the mastic varnish. Interestingly the mastic varnish layer did not appear to inhibit the migration of these oils between layers of paint (Keune 2005).

The use of alternatives to oil binder within the painting composite, such as aqueous based binders for underpainting, has been largely overlooked in the past.

Conservators working with the collection at Mauritshuis now suspect that such aqueous based underlayers may form an important component in 17th century paintings (Noble-Mauritshuis personal communication). Documentary evidence for the use of aqueous based binding media in 19th century oil paintings is substantial (Carlyle 2001a), and there is strong interest in identifying their use in paintings.

A collaborative project with the Getty Conservation Institute and the HART project was initiated by Maartje Witlox (HART) with Tiarna Doherty (Getty) to investigate the imprimatura layer found in Rubens's paintings. This work will be reported in a separate publication (Witlox, Doherty in preparation).

Clear and unequivocal identification of materials which appear between layers of paint or ground (often fluorescing in UV) is still difficult. Few facilities are available for the identification of discrete layers of such minute size outside of the spectroscopic imaging instrumentation developed at FOM-AMOLF in the MOLART and De Mayerne programmes (Heeren *et al.* 2000; Heeren *et al.* 1999; Heeren *et al.* 1996a; Heeren *et al.* 1996b). However recent developments with antibody staining at the Getty Conservation Institute look promising. Samples from the Getty/HART collaboration will be studied to ascertain whether antibody staining can be used to

⁶ The cross-sections were examined under a Zeiss Axioplan 2 microscope at ICN, with UV-light (from a Xenon-lamp and a mercury short arc photo optic lamp HBO, respectively). The filter set UV H365 used for examination in UV-light consists of the following filters: excitation BP 365/12, beam splitter FT 395 and emission LP 397 (BP= bent pass, LP – long pass). Digital photos were taken with a camera attached to the microscope.



Fig. 2. Cross-section of the ground reconstruction at 200x magnification, bottom layer only (no top layer was added over this part). The thin layer fluorescing at the surface is oil which has separated out of the chalk/oil mixture. This indicates that the fluorescing layer in the centre of Figure 1 is an oil layer due to binder separation.

reliably identify not only the presence of proteinaceous material, but the animal source of the protein.

The future of HART Project Reconstructions

It is anticipated that historically accurate reconstructions produced during the HART Project will be important in furthering the accurate interpretation of instrumental analyses performed on cross sections from actual paintings. For example, an artist may have applied an aqueous-based underpainting, then painted with oil over top. It is not known whether subsequent migration of oil from the top layer into the underpainting could contaminate the aqueous-based lower layer. If this does regularly occur, it would lead to the assumption that the underpainting originally contained oil. Similarly it is not known to what extent resinous materials might penetrate through the paint composite from the application of varnish intermediate layers, or from subsequent varnishing. Paint composite reconstructions which reproduce these layering sequences, can refute or confirm assumptions about the permeability and interaction between these individual layers. The effect of contaminants such as glue or wax introduced during conservation treatments can be evaluated using the HART Ground Project reconstructions.

Aside from a visual reference for comparison with cross sections from paintings, because all the materials used in the project are well characterized and consistent, the model paint composites will provide standards for analytical techniques in the future. Another future outcome could be a reference library of images from the paints, paint composites and grounds which could be made available to conservators, conservation scientists and art historians for comparison in the study of cross sections from actual paintings.

Perhaps the most significant outcome of producing historically accurate reconstructions is an advancement in our literacy of paint surfaces -being able to "read" the surface of actual paintings. Information on the flow properties (rheology) of paint during application has always been frozen in dried paint. Comparisons with reconstructed paint take us closer to understanding what we now see in historical works.

Acknowledgements

The HART Report details how individuals and institutions contributed to the project. As there is not enough space here to provide full acknowledgements, this provides a

summary only. The HART project is very grateful to Prof. Dr Jaap Boon at the FOM Institute for Atomic and Molecular Physics (FOM-AMOLF), Alberto de Tagle and his staff at The Netherlands Institute for Cultural Heritage (ICN), to the Netherlands Organisation for Scientific Research (NWO) for their funding, and to the Canadian Conservation Institute (CCI) for lending their support to this project. Staffing was kindly carried out through the help of the Limburg Conservation Institute (SRAL). We owe a special thanks to Anne van Grevenstein and Andrea Retrae for making this possible. We also owe a great debt to Winsor and Newton for their help and advice throughout, particularly to Emma Pearce, Ian Garrett and Alun Foster. Other colourmen assisted significantly for which we were also grateful: Old Holland Classic Oil Paints (Wim van der Zwan, Steve Mills, and José Florenza), Royal Talens (Bert Klein Ovink and Gerwin Pol), and Michael Harding Artist's Colours. We are very grateful to Jef Seynaeve (Belgium) for sharing his expertise on production of traditional Dutch stack lead white and for generous provision of samples. The following companies contributed materials free of charge to the HART project as well as were sharing their knowledge freely with us about their products. We are very grateful to them for their generous assistance: Dhr. Rob le Rütte (VliegentHART BV), and Mr. Philippe Huyvaert (Claessens Artist's Canvases), Mr. Detlef Gysau (Omya), Mr. Frank Bekhuis (Sachtleben) Mr. John Taylor (Dominion Colour Corporation), Dr. Burkhardt Jahn (Grillo Zinkoxide GmbH) and Dr. Annette Kleine (Lukas Artist's Colours). Individuals who contributed to the Hart Project include: Tatiana Ausema, Brian Baade, Robert Barclay, Klaas Jan van den Berg, Hayo de Boer, Maarten van Bommel, Agnes Brokerhof, Meta Chavannes, Mark Clarke, Jane Down, Mireille Engel, David Grattan, Suzan de Groot, Peter Hallebeek, Nanda Harinck, Ralph Haswell, Ella Hendriks, René Hoppenbrouwers, Hans van der Horst, Ineke Joosten, Katrien Keune, Marina van der Lecq, Annelies van Loon, Kees Mensch, Anna van Milligen, Han Neevel, Sylvia Nijhuis, Petria Noble, Nel Oversteegen, Kathrin Pilz, Eric Privee, Ad Stijnman, Bas van Velzen, Lisa Wagner, Bill Wei, Dr. Yokoshima.

References

- Stijnman (2005), Foreword. In: *Art of the Past — Sources and Reconstructions* (M. Clarke, A. Stijnman, and J.H. Townsend eds), Archetype Publishers, London.
- Boon J.J., van der Weerd J., Keune K., Noble P., Wadum J. (2002), *Mechanical and chemical changes in Old Master paintings: dissolution, metal soap formation and remineralization processes in lead pigmented ground/intermediate paint layers of 17th century painting.*, In: *13th Triennial Meeting of ICOMCC in Rio De Janeiro, Preprints* (R. Vontobel, ed). James & James, London. p. 401-406.
- Carlyle L. (1990). "British Nineteenth Century Oil Painting Instruction Books: A Survey of their Recommendations for Vehicles, Varnishes, and Methods of Paint Application." In: *Cleaning, Retouching and Coatings: Technology and Practice for Easel Paintings and Polychrome Sculpture: Preprints of the Contributions to the Brussels Congress, 3-7 September 1990. International Institute for Conservation of Historic and Artistic Works.* London. p. 76-80.
- Carlyle L. (1999). *Paint Driers Discussed in Nineteenth-century British Oil Painting Manuals* *Journal of the American Institute of Conservation* 38, 1 (Spring), p. 69-82.
- Carlyle L. (2001a) *The Artist's Assistant.* Archetype publications, London.
- Carlyle L. (2001b). *MOLART Fellowship, Historical Reconstructions of Artist's Oil Paint: An Investigation of Oil Processing Methods and the Use of Medium-modifiers.* CCI Report No. 72894. Ottawa: Canadian Conservation Institute, revised edition April 2001.
- Carlyle L., Bourdeau J. (1994). *Varnishes: Authenticity and Permanence, Workshop Handbook* (a compilation of traditional varnish recipes and a description of conservator's use of modern varnishes). Ottawa: Canadian Conservation Institute, p.64.
- Carlyle L., Binnie N., van der Doelen G., Boon J.J., McLean B., Ruggles A. (1999). *Traditional Painting Varnishes Project: Preliminary Report on Natural and Artificial Aging and a Note on the Preparation of Cross-Sections.* In: *Fernis, Material Ästhetik Geschichte: International Kolloquium, Braunschweig, 15-17 June 1998* (A. Harmssen ed). Braunschweig: Eine Gemeinschaftsveranstaltung des Herzog Anton Ulrich-Museums. p. 110-126
- Carlyle L., Witlox, M. (2005). *Historically Accurate Oil Painting Reconstructions.* In: *Art of the Past — Sources and Reconstructions* (M. Clarke, A. Stijnman, J.H. Townsend eds). Archetype Publishers, London, 53-60
- CCI Canadian Conservation Institute. *Analytical Research Laboratory Reports 3017.1 and 3017.2.* Ottawa: Canadian Conservation Institute, 1992.
- Cruickshank Smith J. (1924). *The Manufacture of Paint.* London, New York: Van Nostrand Co., p.114, 125-126.
- Groen K. (1997) "Investigation of the Use of the Binding Medium by Rembrandt: Chemical Analysis and Rheology." *Zeitschrift für Kunsttechnologie und Konservierung, Jahrgang 11, Heft 2*, p. 207-227.
- Haswell R., Carlyle L. (2006). *Van Gogh's Painting Grounds: quantitative determination of bulking agents (extenders) using SEM/EDX,* *Microchimica Acta* 155, p.163-169
- Heeren R.M.A., Boon J.J. (1996b). *Rapid Microscale Analyses with an External Ion Sources Fourier Transform Ion Cyclotron Resonance Mass Spectrometer.* *International Journal of Mass Spectrometry and Ion Processes* 157/158, 391-403.
- Heeren R.M.A., van der Weerd J., Boon J.J.. (2000). *FTIR Imaging Spectroscopy for Organic Surface Analysis of Embedded Paint Cross-Sections.* In: *Optics and Lasers in Biomedicine and Culture: Contributions to the Fifth International Conference on Optics within Life Sciences OWLS V, Crete, 13-16 October, 1998* (edited by C. Fotakis, T.G. Papazoglou, and C. Kalpouzou). Berlin: Springer. p. 179-182
- Heeren R.M.A., Boon J.J., Noble P., Wadum J. (1999). *Integrating Imaging FTIR and Secondary Ion Mass Spectroscopy for the Analysis of Embedded Paint Cross-sections.* In: *ICOM-CC Triennial Meeting (12th), Lyon, 29 August - 3 September 1999: Preprints. Vol. I.* London: James & James, p. 228-233.
- Heeren R.M.A., O'Connor P.B., Duursma M.C., van Rooij G.L., van der Hage E.R.E., de Koster C.G., Boon J.J.. (1996a). *FTIR-MS Characterisation of (Co)-polymers.* In: *Proceedings of the 44th ASMS Conference on Mass Spectrometry and Allied Topics, Portland, Oregon.* p. 1101
- Hurst G.H. (1906). *Painters' Colours, Oils, and Varnishes: A Practical Manual.* London, p.43-45
- Keune K. (2005) *Binding medium, pigments and metal soaps characterised and localised in paint cross-sections,* PhD thesis University of Amsterdam, MOLART report 11. p.74
- Kokkori M., Phenix A., Boon J.J. (1999). *Solvent Extraction of Organic Compounds from Oleo-resinous Megilp Paint Media.* In: *Proceedings of the 12th ICOM-CC Triennial Meeting (12th) Lyon (J.Bridgeland).* James & James, London. Preprints vol. 1, p. 318-324

- Lambert T. (1902). *Lead and Its Compounds*. London, p. 126-127.
- Lucanus F. (1829). *Dammar Resin, Concerning the Properties, Chemical Behaviour, and Technical Application* [Translated by the National Gallery of Art Research Project, Mellon Institute, Pittsburgh, Pennsylvania, November 1966.] *Schweigger's Journal* 55, p. 60-66.
- Middelkoop N., Noble P., Wadum J., Broos B. (1998). *Rembrandt under the scalpel The Anatomy Lesson of Dr Nicolaes Tulp Dissected, The Hague/Amsterdam*, p. 66
- Muckley W.J. (1882). *A Handbook for Painters and Art Students on the Character and Nature and Use of Colours*. London, p. 2-4.
- Noble P. (1999). *Technical description, Rembrandt, Head of a man in a plumed hat, Mauritshuis Conservation Studio. The Hague*
- Noble P., Wadum, J., Groen K., Heeren, R., Van den Berg K.J. (2000). *Aspects of 17th century binding medium: inclusions in Rembrandt's Anatomy Lesson of Dr Nicolaes Tulp Art & Chimie, la couleur. Actes du congrès, Paris*, p. 126-129.
- Olby J.K. (1966). *The Basic Lead Carbonates. Journal of Inorganic and Nuclear Chemistry* 28, 2507-2512.
- Shoemith D.W., Bailey M.G., Taylor P. (1988). *Anodic Oxidation of Lead in Aqueous Carbonate Solutions. II. Film Formation and Dissolution in the pH Range 9 to 14. Canadian Journal of Chemistry* 66, p. 2941.
- Stewart A. (1950). *Lead Pigments and Paints. Official Digest (Federation of Paint and Varnish Production Clubs), December*, p. 1100.
- Stewart A. (1950). *Lead Pigments and Paints. Official Digest (Federation of Paint and Varnish Production Clubs), December*, p. 1100.
- Tétrault J., Sirois J., Stamatopoulou E. (1998). *Studies of Lead Corrosion in Acetic Acid Environments. Studies in Conservation* 43,17-32.
- Thickett D. (1997). *Relative Effects of Formaldehyde, Formic and Acetic Acids on Lead, Copper and Silver. Report No. 1997/12. London: Conservation Research Group, The British Museum*, 29, August.
- Townsend J.H. (1993). *The Refractive Index of Nineteenth Century Paint Media: A Preliminary Study. Proceedings of the 10th ICOM-CC meeting in Washington (J.Bridgeland ed), James and James, London. Preprints Vol. II*, p. 586-591.
- Townsend, J.H. (1994). *Whistler's Oil Painting Materials. The Burlington Magazine*, CXXXVI, p. 690-695.
- Townsend J.H., Carlyle L., Burnstock A., Odlyha M., Boon J.J. (1998). *Nineteenth-Century Paint Media: The Formulation and Properties of Megilps. In: Painting techniques history, materials and studio practice. (A. Roy and P. Smith eds) IIC Dublin meeting, International Institute for Conservation of Historic and Artistic Works, London*. p. 205-210
- Van den Berg J. D. J., Vermist N. D., Carlyle L., Holcapek, M., Boon J.J. (2004). *Effects of traditional processing methods of linseed oil on the composition of its triacylglycerols, Journal of Separation Science*. 27, 181-199.
- Van den Berg J.D.J (2002). *Analytical Studies on Traditional Oil Paint. PhD thesis University of Amsterdam. Report of MOLART Series: MOLART 6.*
- Van den Berg, K.J., van der Horst J., Boon J.J. (1999). *Recognition of Copals in Aged Resin/Oil Paints and Varnishes." In: 12th ICOM-CC Triennial Meeting Lyon (J. Bridgeland ed). James & James, London. Preprints, Vol. II*. p. 855-861.
- Van der Weerd J., Boon J.J., Geldof M., Heeren R.M.A., Noble P. (2002). *Chemical changes in old master paintings: dissolution, metal soap formation and remineralization processes in lead pigmented paint layers of 17th century paintings. Zeitschrift für Kunsttechnologie und Konservierung*, 16, p. 36 - 51.
- Van der Wetering E. (1997). *Rembrandt, The Painter at Work. Amsterdam University Press, Amsterdam*. p. 239-240.
- Vermist N.D. (2000). *Analytische karakterisering van traditioneel bereide lijnzaadolie en olieverb. Stageverslag (Internship Report). Afstudeerverslag/(Undergraduate Thesis). Hogeschool Alkmaar, Institute voor Laboratorium-onderwijs, Alkmaar (NL).*
- Woodcock S.A. (1995). *The Roberson Archive: Content and Significance. In: Historical Painting Techniques, Materials, and Studio Practice: Preprints of a Symposium, University of Leiden, the Netherlands, 26-29 June 1995. Marina del Rey, CA: The Getty Conservation Institute* p. 30-37.

Various approaches to Van Gogh technical studies; common grounds?

THE PAINTING MATERIALS AND TECHNIQUE OF VAN GOGH

Abstract:

This paper takes the study of Van Gogh's Paris picture supports (canvases, *cartons* and priming layers) as a common theme of investigation. The topic was examined from different angles, reflecting the multidisciplinary approach of the De Mayerne Programme. Dr. Stéphanie Constantin conducted a detailed search for documentary and archival information in Paris relating to the manufacture and retail of artist materials in late nineteenth century France, with a focus on Van Gogh's suppliers. Put together with evidence derived from the technical examinations of his Paris paintings, these documentary findings helped to reconstruct the artist's working practice in the period. All of the listed colormen he used are known to have supplied other Impressionist and Post-Impressionist painters too, making it probable that Van Gogh used some of the very same materials as his contemporaries. Beatrice Marino at AMOLF conducted an in-depth imaging analytical study of ground/paint samples from a group of Paris pictures painted on ready-primed *carton* supports with a broader aim was to develop quantitative techniques for comparing and classifying paint cross-sections. Within the HART project led by Dr. Leslie Carlyle, precise reconstructions of a selection of Van Gogh's prepared picture supports and paints were made. Some Paris examples illustrate how these help to understand the working properties and visual consequences of using these materials.

¹ Van Gogh Museum, Postbus 75366, 1070 AJ Amsterdam, hendriks@vangoghmuseum.nl

² 149 rue Ordener, 75018 Paris, stephanie.bennett@wanadoo.fr

³ FOM Institute-AMOLF, Kruislaan 407, 1098 SJ Amsterdam, marino@amolf.nl

Fig. 1. Table of colourmen visited by Van Gogh in Paris (1886-1888), reproduced from Hendriks 2007. Information on colourmen stamps on Van Gogh paintings was given by Luuk Struick van der Loeff at the Kröller-Müller Museum in Otterlo, and by Kristin Hoermann- Lister at The Art Institute of Chicago.

Table 1. PAINT-SELLERS VISITED IN PARIS

Information on companies was compiled from the Paris editions of *Didot-Bottin, Annuaire-Almanach du Commerce, de l'Industrie, de la Magistrature et de l'Administration*, sharing the results of archival research conducted by Stéphanie Constantin.

Trade stamps/labels	Company name	Retail address in the period 1886-88	Dates of company	Listing
F 322, Vase with lilacs, daisies and anemones, stamp on back of canvas (Genève Musée d'art et d'histoire)	Dubus	Boulevard Malesherbes, 60	1877-1898	Specially for painting and drawing
F 215b, Portrait of Agostina Segatori, stamp on back of canvas (Van Gogh Museum, Amsterdam)	A. Fermine	Rue Notre-Dame-de-Lorette, 37	1876-1911	Easel-maker: mannequins, easels, maquettes
F 324, Vase with cornflowers and poppies, stamp on back of canvas when still on original strainer, recorded in photo made before the painting was lined (private collection)	Hardy-Alan	Rue du Cherche-Midi, 36	1868-1920	Colours: painting dealer (from 1877): canvases (from 1884): easels (from 1894): painting and print restorer (from 1906)
F 380, Self portrait, stamp on back of carton support, (Kröller-Müller Museum, Otterlo): F378, Basket of apples, stamp on back of canvas (Kröller-Müller Museum, Otterlo)	Gust. Hennequin	Avenue de Clichy, 11	1874-1903	Colours, canvas & brushes
Former label recorded on back of Dante's Death Mask (inventory number v3 V/1994, Van Gogh Museum, Amsterdam)	Louis Latouche	Rue Lafayette, 34	c.1870-1887	Colours
F 266a , Sunset in Montmartre, stamp visible through lining canvas (Van Gogh Museum, Amsterdam): F 273, Windmills on Montmartre, stamp on back of canvas (Bridgestone Museum of Art, Tokyo)	Hofer Frères (ancienne maison Vallé fondée en 1770)	Grands-Augustins, 3	1770-1890	Colours: painting canvases: photographic accessories: painting dealer, expert and restorer (1888)
F 215d, Portrait of a woman, stamp on back of canvas still on its original strainer (Van Gogh Museum, Amsterdam)	Rey et Perrod	Rue de la Rochefaucauld, 51 (also shop at Rue Notre-Dame-de-Lorette, 64)	1868-1905	Fine colours
Labels on the backs of carton supports: F 216a, F 216b, F 216c, F 216e, F 216f, F 216j, F 231, F 243a (Van Gogh Museum, Amsterdam).	Pignel- Dupont	Rue Lepic, 17	1883-1895	Colours and wall papers
No stamps or labels known	J.-F. ("père") Tanguy	Rue Clauzel, 14	1874-1894	Fine colours
F 118, Still life with potatoes, stamp on back of original canvas transcribed onto lining canvas (Museum Boijmans Van Beuningen, Rotterdam): F 382, Still life with grapes, stamp on back of canvas (The Art Institute of Chicago): F 452, Four sunflowers run to seed, stamp on original stretcher (Kröller-Müller Museum, Otterlo): F 373, The Courtesan (copy after Eisen), stamp on original stretcher (Van Gogh Museum, Amsterdam)	Tasset et L'Hôte	Rue Fontaine-Saint- Georges, 31	1887-1910	Colours

Introduction

This highlight paper focuses on findings that relate to the period when Van Gogh lived and worked in Paris from 1886 to 1888. For art historians this part of his oeuvre poses particular problems. At the time Vincent lived with his brother Theo and therefore had no need to correspond, depriving us of the letters and paint orders that are usually such a rich source of information on his creative goals and working procedures. Moreover, it was a period of enormous technical and artistic experimentation, producing works that widely fluctuated in terms of style and technique within a narrow space of time. Together this has complicated the task of making a plausible reconstruction of his Paris oeuvre, and left openings for debate on issues of attribution and chronology. Given this context, information on the materials and techniques employed by the painter take on added importance to help resolve these questions.

Documentary sources

A wide range of sources was consulted by Stéphanie Constantin for her research on the manufacture and retail of artist materials in late nineteenth century France, which included artists' correspondence, painters' manuals, contemporary business directories (*Almanachs du commerce et de l'industrie*), historical scientific reviews, colourmen patents, and liquidation sheets compiled in the event of traders facing financial difficulty or bankruptcy. This new found information, put together with evidence gleaned from technical examination of Van Gogh's Paris picture supports for a forthcoming catalogue of the Van Gogh Museum collection, has reformed our view of the artist's working procedure in the French capital (Hendriks and Van Tilborgh, 2006; Hendriks, 2007).

In other periods of his working career, Van Gogh is known to have purchased canvas by the meter, cutting the lengths of fabric into pieces that were combined with loose stretchers to manufacture picture supports (Van Tilborgh and Vellekoop, 1999; Lister et al. 2001; Hendriks and Van Tilborgh 2001). However, this investigation of his Paris paintings demonstrated that his procedure in the French capital ran counter to that of other periods investigated so far. A partial inventory of colourman stamps and labels on the backs of canvas and *carton* picture supports revealed that they had been purchased ready-made from various shops instead. Eight different addresses are recorded, all fairly small businesses established in and around Montmartre (Fig. 1). In addition, there is written evidence for dealings with the colourman and art dealer père Tanguy, who does not seem to have marked the materials he sold. The idea that Van Gogh purchased his commercially prepared canvases individually from a variety of sources is backed up by the endless variation in the physical characteristics of his Paris canvases examined in the collection of the Van Gogh Museum. Bearing in mind that this comparative technical study encompassed only approximately half his oeuvre, it strongly suggests that Van Gogh took advantage of the wide ranging types on offer in the artist quarters of Montmartre.

Studies were conducted to trace the histories of these companies visited by Van Gogh, consulting the Paris editions of the *Annuaire et Almanach du Commerce et de*



l'Industrie. It emerged that none of the colourmen he patronised were especially renowned for the quality of the products they sold, and aside from Tasset et L'Hôte and père Tanguy, nor were they particularly well known. Evidently Van Gogh chose proximity in favour of reputation or quality, simply visiting shops close at hand. For example, trade stamps surviving on the backs of pictures made just before and straight after his move from 25 rue Laval (currently Rue Victor Massé) to 54 Rue Lepic in June 1886, reveal that in each case he had purchased the picture supports from shops located around the corner from his living address at the time. Certainly another determining factor for his choice of suppliers, as his earlier and later correspondence makes abundantly clear, would have been the wish to economise on the cost of his painting materials. Technical examinations and analysis of his Paris pictures has repeatedly shown the use of low grade, presumably cheaper materials that have degraded in the course of time (Hendriks 2007; Burnstock et al. 2005; Van Bommel et al. 2005).

This study of documentary sources on Van Gogh's suppliers also reminds us of the shady area that existed between the manufacture and retail of artist materials sold in the period. Only two of the colourmen supplying Van Gogh are officially recorded as being manufacturers, as opposed to just retailers of the products they sold: Hardy-Alan and Hofer frères. However, listings in the trade almanac may not have been entirely trustworthy in this respect. For example an 1885 inventory of the shop of Pignel (precursor of Pignel-Dupont visited by Van Gogh) recorded the presence of pestles and mortars, a colour mill and tube-filling machine. Evidently though not listed as a manufacturer, Pignel was well equipped to process materials at the client's request, or to diversify their range. Conversely, although Tasset et L'Hôte was listed as a 'manufacturer' in the *Almanac*, there is no evidence for a large premises (the shop measured only 20 m² according to the *états cadastraux* of 1876) or associated factory for this purpose. Branded *marque de fabriques* from the company Bourgeois aîné,

Fig. 2. Paul Signac, *Le Port de Portrieux*, op. 182, 1888, (private collection). Detail of Tasset et L'Hôte trade stamp on the stretcher, with a branded *marque de fabrique* from the firm *Bourgeois aîné* adjacent. Photograph by E. Hendriks.



discovered on some of the keyed stretchers stamped by Tasset et L'Hôte, do provide evidence for some kind of joint operation however (Fig. 2). It is known that firms could simply purchase a registered *marque de fabrique* bearing the company name and logo, to mark merchandise that was manufactured elsewhere.

Putting together these facts so far, leads to two main conclusions. Firstly, the suppliers of Van Gogh's painting materials in Paris were more numerous and less well documented in the letters than for other periods of his production. Though already dealing with Tasset et L'Hôte and père Tanguy, his principal suppliers from late Arles on, evidently Van Gogh shopped around and visited several other addresses in Montmartre. All of the listed colourmen he used are known to have supplied other Impressionist and Post-Impressionist painters too, making it probable that Van Gogh used some of the very same materials as his contemporaries. This highlights the relevance of studying his painting materials. Secondly, the chain of events that took place through the different stages of manufacture to retail of the paints and picture supports bought by Van Gogh is likely to have been complex and variable. Together these factors complicate the search for unique and consistent physical characteristics that might help to discriminate the materials used in his Paris pictures, for purposes of dating or attribution for example.

Quantitative imaging analysis of ground paint cross-sections

Recent technical-art historical studies on Van Gogh have demonstrated that it is useful to group associated pictures according to a shared set of materials. One example is the possibility of matching up picture supports that were cut from the same roll of primed canvas, which consequently show an identical fabric weave and ground, as a basis for reconstructing his later French oeuvre (Lister et al. 2001; Hendriks and Van Tilborgh 2001). Study of his Paris paintings has disclosed the presence of matching intermediate ground layers too, used to cover up failed works and prepare the picture supports for reuse (Hendriks, 2007). Again, since the artist generally used up his supports quickly one after the other, this usually points to a close date of origin for the final pictures made.

In all these studies, the method used to establish a 'match' between paintings has involved a detailed, largely qualitative comparison of the physical characteristics and material composition of the supports (canvas or *carton*) and grounds.

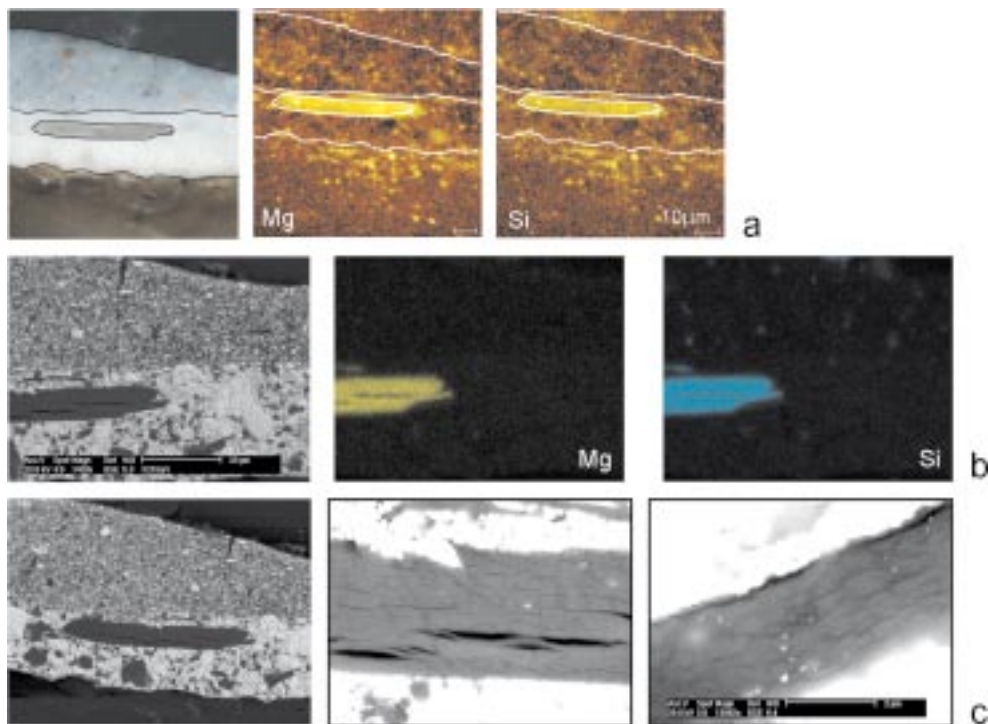
This pilot study took, as its theme, a test series of ground samples from nine Paris pictures painted on *carton*. The paintings in question were six studies of plaster-cast

statuettes (F nos. 216a, 216b, 216d, 216e, 216f, 216j in De la Faille, 1970) and three small portraits (F nos. 267, 294, 296), dated to mid June 1886 and to 1887 respectively on the basis of subject matter and style. Trade labels surviving on the back of the mid June 1886 plaster cast studies provide evidence for the provenance of materials, recording the shop address of Pignel-Dupont established in the Rue Lepic where Van Gogh had moved to earlier that month. Physical evidence suggested that the picture supports had been cut from larger ready-primed sheets, and the use of a standard type of cardboard (a 2mm thick, 2-ply pasteless board manufactured from unrefined wood pulp) and consistent ground formulations likely indicate a common source of manufacture. The primed supports could be divided into two main groups, according to their surface colour and the related material composition of the grounds. Based on light microscopy and SEM-EDS analysis of ground sample cross-sections, different formulations emerged for a pale-grey, and a white type of ground, corresponding to the two colours of preparation mentioned in nineteenth-century sources. The main difference between them is that the pale-grey grounds show a more elaborate composition than the white ones, with barium sulphate and gypsum supplementing or replacing chalk as fillers for the lead-white based paints. In this case it was not deemed possible to further discriminate separate batches of ground application, based upon slight variations in the composition of samples, or microscopic features of ground surface texture for example.

The study by Marino (Marino 2006, Marino 2005a,b) examined the same set of ground samples, adding a random control sample of ground from an 1887 portrait on canvas (F 369). One aim was to ascertain salient features that could more effectively discriminate between closely similar ground paint cross-sections. Image processing and pattern recognition techniques were employed to enhance and extract this information from samples. Furthermore, quantifying software was used to ascertain the degree of similarity for each of these features in an accurate and reproducible way. The features considered were: the colour content of light microscopic images of samples, the structure and texture of the paint characterised by particle size distribution in SIMS images and the material (elemental and mineralogical) composition of ground paints derived from imaging SIMS data.

Colour content analysis was able to divide the grey-primed supports into two different groups used for the 1886 and 1887 pictures respectively (F 216d, 216e, 216f, 216j, and F 267, 294, 296). The two white-primed supports (F 216a and 216b) aligned more puzzlingly however, split between both groups, whereas the control sample (F 369) formed a separate category as one might expect. The different classification of samples achieved by comparing the colour content of microscopic images may be explained by the complex way in which colour is related to material composition. Colour depends upon light refraction that is affected by features such as particle size, refractive index of material components and surface roughness of the paint film (Marino et al, 2005). In this study the texture of the ground paints was considered to be a highly discriminating feature, so that the lack of similarity between samples showed that no one pair belonged to exactly the same batch of ground preparation. Moving on to material composition, SIMS distribution maps identified new mineralogical features as highly significant markers for the paint although the main

Fig. 3. The composition of a Menilite opaline silica particle in the ground from Plaster figure of a female torso by Van Gogh (sample code F216a/1) visible in the light-microscopic image is illustrated with maps of silicium and magnesium by SIMS (a) and SEMEDX (b). The BSE images of the particle at higher magnification (c) reveals a laminated structure of the particle. Menilite occurs in the Ludian (Eocene) marls between the two gypsum masses in the Paris basin (see Marino 2006).



elemental composition of all the ground samples is similar. These included particles with strontio-baryte, and, unusual elongated particles of menilite, a magnesium-rich variety of opaline silica (Marino et al. 2005; Marino 2006) (Fig. 3). The latter points to the specific origin of source materials from the Paris basin, and the likelihood that at least some of the materials present in the grounds already co-existed in particular sediment layers mined in that region, rather than being separate and deliberate additions by the manufacturer. These joint findings took us beyond the conclusions that could be made by the initial qualitative analysis.

A general observation to be made from this case study is that a quantitative classification of samples may only partly follow that made using qualitative criteria. This can be explained by the fact that different features were considered in each case, but also by the fact that similar features may be weighted differently according to the approach. As for conventional connoisseurship, to draw appropriate conclusions from this cumulative data depends upon the ability of the paint specialist to weigh the significance of the various types of evidence gathered. Samples were assigned to different groups depending upon the particular criteria considered and the weighting these were given. This new method for a quantitative characterisation of paint

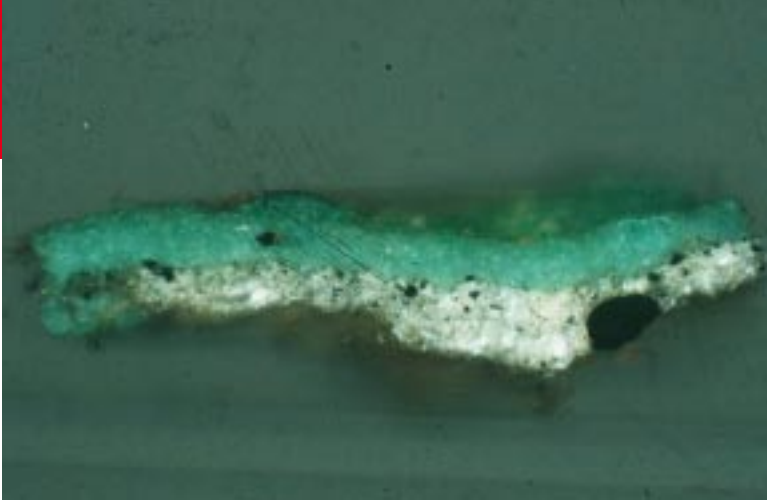


Fig. 4. The bridge in the rain; after Hiroshige, October-November 1887, (Vincent van Gogh Foundation) Van Gogh Museum, Amsterdam. Paint cross-section showing the c. 0.05 mm thick ground layer that contains chalk and bone black. The thin layer of emerald green with gypsum on top is from the decorative border of the painting. Photograph by M. Geldof, The Netherlands Institute for Cultural Heritage, Amsterdam.

samples is envisaged as a complementary tool, supplementing the traditional qualitative approach. Potentially it enables a more systematic analysis of microscopic features in ground and paint samples, in order to understand how these relate to the visual and working properties of these materials for example, or to aid a classification of the materials used by different schools, or painters, at different moments in time. Viewed within the broader context of advanced painting studies, it is interesting to note the development of analogous digital methods to aid the painting expert in his analysis of macroscopic features of painting technique, such as the complementary colour contrasts and brushwork texture evident in paintings by Van Gogh (Berezhnoy et al. 2005; Berezhnoy et al. 2006, in press).

HART reconstructions

A third approach taken towards the investigation of Van Gogh's primed picture supports has involved making historically accurate reconstructions in collaboration with De Mayerne's HART project (Carlyle et al, 2006). Whilst the set-up and findings of this project are described in full elsewhere, this paper considers just three examples that demonstrate how the exercise of making these reconstructions has improved our understanding of the working properties of these materials and the visual consequences of using them.

The first example entails the reconstruction of a double layered type of commercial ground, consisting of a layer of lead white-in-oil, on a thin layer of chalk-in-glue. So far this particular type of ground has been found in ten Paris pictures. In all but one of these examples the ground had been applied to skeletal weave canvases that averaged only 11.5 – 13.5 thin threads per cm. Comparison with sales book samples of artists' canvas suggest that this gauze-like canvas was probably equivalent to a low *étude* or *ordinaire étude* grade. The question was why this type of ground was



Fig. 5. HART reconstruction showing dark staining of the grey chalk ground caused when brushstrokes were applied on top.

usually found combined with this particular type of canvas. On the one hand, it seemed logical that the first chalk-in-glue layer of the ground would function as a cheaper and faster drying material to fill the wide pores of the fabric, compared to the lead white-in-oil paint used on top. But HART replica's using a canvas of comparable open weave demonstrated that the chalk-in-glue mixture was surprisingly economic in use too, since there was no evidence for wastage in the form of beads of ground squeezed through the weave interstices to the back of the canvas during the process of application, regardless of whether the canvas had been sized in advance with liquid or gelled glue, or even left unsized.

The second example entails a reconstruction of a chalk-in-glue priming, coloured light grey by additions of bone black pigment. This specific ground has been identified in *The bridge in the rain; after Hiroshige*, dated to October-November 1887, applied as a very thin and uneven layer onto fine, tabby weave linen (averaging 19.1 x 19.0 threads per cm) (Fig. 4). This was one of the new types of absorbent substrate that Van Gogh experimented with around this time, alongside the traditional types of artists' canvas prepared with lead white-in-oil based grounds. Most likely, as for other painters of his day, Van Gogh considered the advantage of absorbent supports to lie in the fact that, by reducing the oil content of the paint, they would render the colours more brilliant and less subject to change caused by darkening or a reaction of the oil medium. The HART reconstruction demonstrated just how effective the chalk ground was in this respect. Immediate staining resulted when impasto brush marks were applied on to the ground as the oil medium wicked out and spread to form blackish halo's around their periphery (Fig. 5). This finding inspired us to look again at *The bridge in the rain*, revising our interpretation of the visual data. Examination of the tacking margins provided new evidence for the fact that Van Gogh had 'oiled out' the light grey surface of his canvas before use, presumably to circumvent the staining effect that would otherwise occur each time a separate brushstroke was applied. It is



this original feature of Van Gogh's technique that seems to be the principal cause of blackening of the ground, rather than the impact of later wax lining and varnishing treatment as had previously been assumed.

The last example entails an unusual type of ground with coarsely ground particles of barytes as its single pigment ingredient; identified in a growing body of works that includes four late 1887 Paris pictures by Van Gogh (Hendriks, 2007, and for F 452 see Ten Berge et al, 2002), as well as several works painted by Van Gogh and Gauguin in the period October to December 1888 when sharing a studio in Arles (Lister et al, 2001). In every instance the colour of the ground is beige, unlike the white barium sulphate ground found on a portrait made in the immediate circles of Gauguin (Hale, 2002). Early documentation on Van Gogh's *Self-portrait* (F 344) records the opinion that the barytes ground was initially white, but had been stained beige by wax-resin lining. Here it is argued that colour is mainly determined by the original materials used, including the particular grade of barite pigment. Trace elements of silicon, iron, calcium, potassium and aluminium were detected by SEM-EDS analysis of ground samples (Lister et al. 2001; Hendriks 2007), present as earth impurities such as iron oxides that are commonly associated with a low grade of the natural mineral and known to give it a pinkish cast (Feller 1986). Furthermore, HART reconstructions demonstrated how the particular binding medium used will have a crucial impact upon the colour of the ground. A rather pure grade of barium sulphate in an animal glue medium provided a white film, whereas mixing exactly the same barium sulphate with an animal glue and oil emulsion provided a greenish-beige film, and with oil a dark brownish-beige one. So far sample analysis has shown Van Gogh's preference for a mixed animal glue and oil binding medium, which is consistent with this idea (Lister et al. 2001; Hendriks 2007). Though practical and economic issues must have played an important part in the choice of these particular priming materials, clearly the resulting beige colour of the ground was also used to pictorial advantage in the works considered.

These three examples serve to illustrate the essential types of information that historically accurate composite reconstructions can provide, informing our interpretation of what we see on the actual paintings. Moreover, the HART reconstructions made for this project provide a valuable resource for future research. One possibility would be a systematic study on the darkening effects of wax-resin lining and varnishing treatments for different types of substrate, helping to understand the visual impact of such interventions that have been carried out on a broad scale.

Conclusion

In the Van Gogh project of the De Mayerne Programme, an interdisciplinary approach was followed to investigate different aspects of the artist's working methods in relation to contemporary practice. One example was a joint study conducted on the ageing properties of his red lake paints (see chapters by Van den Berg et al. and Carlyle in this volume). This highlight paper takes the topic of picture supports as its common theme, once again, demonstrating how fruitful such an approach can be. The museum experienced how this type of research is of great interest to both a general and specialist audience alike, lending itself to presentation in various forms that range from museum exhibits to scholarly collection catalogues.

Acknowledgements

The De Mayerne study built upon recent results from a broad campaign of technical research conducted for a forthcoming catalogue of Antwerp and Paris paintings in the collection of the Van Gogh Museum, involving collaboration between the Van Gogh Museum, The Netherlands Institute for Cultural Heritage (ICN) and Shell Research and Technology Centre in Amsterdam (SRTCA). Thank you in particular to Muriel Geldof, Kees Mensch and Natasha Duff for their contributions to this research.

References

- Berezhnoy I., Postma E. O., Van den Herik J., (2006) *Computer Analysis of Van Gogh's Complementary Colours*. In: *Pattern Recognition Letters Journal*, in press.
- Berezhnoy I., Postma E. O., Van den Herik J., (2005). *Computerized Visual Analysis of Paintings*. In: *Proceedings 16th International Conference of the Association for History and Computing*, p. 28-32.
- Burnstock A., Van den Berg K.J., Carlyle L., Clarke M., Hendriks E., Kirby J., Lanfear I. (2005). *A comparison of the fading and surface deterioration of red lake pigments in six paintings by Vincent van Gogh with artificially aged paint reconstructions*. In: *Proceedings of the 14th Triennial Meeting of the ICOM Committee for Conservation in The Hague*, vol. 1. James and James, London. p. 459-466.
- Carlyle L., 2006 (this publication)
- De la Faille J. -B. (1970). *The works of Vincent van Gogh; his paintings and drawings*, Meulenhoff International Amsterdam, 697 pp..
- Feller R. L. (1986). *Barium Sulphate - Natural and Synthetic*. In: *Artists' Pigments; a Handbook of their History and Characteristics* (Feller R. ed). National Gallery of Art, Washington, vol. 1, p. 47-64.
- Hale C. (2002). *Gauguin's paintings in the Metropolitan Museum of Art; recent revelations through technical examinations*. In: *The Lure of the Exotic; Gauguin in New York Collections* (C. Ives and S. A. Stein, with C. Hale. and M. Shelley). The Metropolitan Museum of Art, New York, p. 175-195.
- Hendriks E. (2007). *Van Gogh's working practice; a technical study*. In: *Vincent van Gogh Paintings; Antwerp and Paris (1885-1888)* (Van Tilborgh, L. and Hendriks, E.), vol. 2. Van Gogh Museum,

- Waanders, Zwolle, ca. 450 pp.
- Hendriks E., Van Tilborgh L. (2006). *New Views on Van Gogh's Development in Antwerp and Paris; an integrated art historical and technical study of his paintings in the Van Gogh Museum*. PhD dissertation University of Amsterdam
 - Hendriks E., Van Tilborgh L. (2001). *Van Gogh's 'Garden of the asylum'; genuine or fake?* In: *The Burlington Magazine*, volume CXLIII. p. 145-155.
 - Lister K., Peres C., Fiedler, I. (2001). *Tracing an interaction; supporting evidence, experimental grounds*. In: *Van Gogh and Gauguin; The Studio of the South* (D. Druick and P. Kort Zegers), *The Art Institute of Chicago*. p. 364-366.
 - Marino B. (2006). *Paints quantified: Image analytical studies of preparatory grounds used by Van Gogh*, PhD dissertation University of Amsterdam.
 - Marino B., Hendriks E., Boon J.J. (2005). *Quantitative colour comparison of grounds and paint cross-sections from a selection of paintings from the Paris period by Vincent van Gogh*. In: *Proceedings of the 14th Triennial ICOM Committee for Conservation Meeting in The Hague* (I. Vergier ed), vol. 1. James and James, London. p. 814-823.
 - Marino B., Keune K., Hendriks E., Boon J.J. (2005). *SIMS studies of the material aspects in grounds and paints in paintings by Van Gogh*. In: *Proceedings of Art'05- 8th International Conference on Non Destructive Investigations and Microanalysis for the Diagnostics and Conservation of the Cultural and Environmental Heritage, Lecce, Italy, 15- 19 May, 2005*.
 - Van Bommel M., Geldof M., Hendriks E. (2005). *An investigation of organic red pigments used in paintings by Vincent van Gogh (November 1885 to February 1888)*. *Art Matters* 3, Waanders, Zwolle, p.111-137.
 - Ten Berge J., Meenendorp T., Vergeest A., Verhoogt R. (2003). *The paintings of Vincent van Gogh in the collection of the Kröller-Müller Museum, Otterlo* (T. van Kooten, M. Rijnders eds.). Kröller-Müller Museum, Otterlo.
 - Van Tilborgh L., Vellekoop M. (1999). *Vincent van Gogh Paintings; Dutch period (1881-1885)*, vol. 1, Van Gogh Museum, Waanders, Zwolle.

Fading of red lake paints after Vincent van Gogh – an interdisciplinary study involving three De Mayerne projects

HART, VAN GOGH AND MM19

Abstract:

Seventeen lake pigments and 100 lake paints were made following 19th-Century English and French recipes and based on analytical studies of red lake paints from works by van Gogh. The relatively small scale of the experiments raised some problems in making of historically accurate pigments and paints; yet accelerated ageing behaviour of the reconstructions gave similarities to phenomena observed on the actual paintings. Light ageing of the paints indicated that the synthetic pigment eosin, very popular in Vincent's time, fades much faster than other lakes used by Vincent van Gogh. Lakes made from madder, Kopp's purpurin and cochineal on alumina faded more slowly than those made from brasilwood, eosin, and cochineal on tin. Total fading of the latter pigments occurred within the equivalent of 10 years of light exposure under museum conditions (by reciprocity). Discoloration was intensified by thin application and by admixture with lead white. A pilot experiment indicated that the rate of fading may be reduced by UV and oxygen exclusion.

¹ Instituut Collectie Nederland, PO box 76709, 1070 KA Amsterdam, The Netherlands, Klaas.Jan.vd.Berg@icn.nl

² Courtauld Institute of Art, Strand, London, WC2R 0RN, England, Aviva.Burnstock@courtauld.ac.uk

³ Tate Britain, Millbank, London, SW1P 4RG, England, leslie.carlyle@tate.org.uk

⁴ Hamilton Kerr Institute (Fitzwilliam Museum), University of Cambridge, Whittlesford, Cambridge, CB2 4NE, England, mark@clericus.org

⁵ Van Gogh Museum, PO box 75366, 1070 AJ Amsterdam, e.hendriks@vangoghmuseum.nl

⁶ Stichting Restauratieatelier Limburg, Daemslunet 1c, 6221 KZ Maastricht, SRAL@wx.nl

⁷ National Gallery, Trafalgar Square, London, WC2N 5DN, England, Jo.Kirby-Atkinson@ng-london.org.uk

Introduction

The fading and discoloration of the red lake pigments used by Vincent van Gogh, especially in his late paintings made in southern France has been documented by several authors (Hendriks and van Tilborgh (2001) and references cited therein). More recently, severe colour changes, due to the fading of the organic red pigments and the surface deterioration of these pigments, have been noted in paintings by van Gogh from his Antwerp and Paris periods. Van Bommel et al. (2005) identified madder, cochineal and redwood in a number of these paintings. In some instances two lake pigments were found together, but redwood was never used by itself. Eosin has been found several times in Vincent's later works (M. Geldof et al., unpublished results).

To investigate the behaviour of red lakes in more detail, an interdisciplinary collaborative effort was initiated and coordinated by the MM19 group at ICN and the Courtauld Institute of Art within the framework of three De Mayerne Programme components i.e. MM19 (CPI Van den Berg), HART (CPI Carlyle) and Van Gogh (CPI Hendriks) who partnered with the Courtauld Institute of Art and National Gallery in London. Historical accuracy in the production of the reconstructions of lake pigments and paints was warranted by Jo Kirby and Leslie Carlyle. Artificial ageing was carried out at SRAL and the fading and surface deterioration characteristics of the reconstructions were compared with six works by Van Gogh from his Paris and Antwerp periods studied by the team of the Van Gogh Museum in Amsterdam. Some results of the red lake project have been published earlier (Kirby 2005; Burnstock et al. 2005a).

In the present study the formulation of lake pigments from contemporary recipes, making of paint reconstructions and their subsequent artificial light ageing are described with a special focus on the relative rates of fading of the paints. The red lake paints are further studied at ICN using HPLC and light microscopy in combination with UV/VIS spectroscopy to examine degradation products, effects of oxygen exclusion on fading and depth of fading. Cross sections from this project and paintings by van Gogh and contemporaries are compared to further evaluate the historical accuracy of the reconstructions. A study of the photochemistry of fading of the different lake pigments is carried out at by the New University, Lisbon by Melo and Pina and co-workers.

Experimental section

Materials, light ageing and colour measurement

Materials used are given in Table 1. Paint reconstruction samples were light-aged at the Stichting Restauratie Atelier Limburg (SRAL). Illumination was provided by fluorescent lamps, output 10,000 lux at sample surface. The total ageing time of 2850 hrs is calculated to be equivalent to 49 exhibition years under recommended museum conditions (200 lux, eight hours a day, assuming reciprocity), or to more than 64 years of ageing in the van Gogh museum, where paintings are illuminated at 150 lux. Colour changes were recorded at intervals during ageing; observer 2°, illuminant D65, specular component excluded. Data consist of the average of three measurements on

three spots, converted to CIE 1976 L*a*b* space. More detailed descriptions of techniques are given in (Burnstock et al. 2005a).

Red lake pigment reconstructions

In a workshop co-ordinated by Kirby, seventeen red lake pigments were made using selected 19th-century recipes, including paint technology manuals and, in the case of the madder pigments, scientific papers describing the extraction of the colouring matters. French sources were used where possible, supported by English and German documents (Kirby 2005).

Materials and procedures are summarised in Table 1. Lakes were made from the dyestuff extracted from cochineal (*Dactylopius coccus* Costa) on tin- and aluminium-containing substrates, including a tin-containing lake with a starch extender (C4): this combination was found in paintings by van Gogh, Seurat and Renoir (Van Bommel et al. 2005, Kirby et al. 2003, Burnstock et al. 2005b). Lakes prepared from madder (*Rubia tinctorum* L.) dyestuff on aluminium-containing substrates included one from laboratory-prepared Kopp's purpurin (M2), which contains little alizarin and some elemental sulphur (probably present as sulphate). M2 was designed to be rose-pink: madder lakes of this colour were widely available and Kopp's purpurin, used in France until about 1900, was a likely starting material. As brasilwood dyestuff (from *Caesalpinia* sp.) was present with madder dyestuff in some paint samples examined, a lake containing a mixture of these two dyestuffs was prepared (BM). Eosin lake was prepared on an aluminium-containing substrate, using a lead salt as precipitating agent.

Problems encountered in filtering and grinding some of the pigments were partly the result of inevitable compromises made when scaling down preparations originally manufactured on a large scale. The physical properties of precipitated pigments (particle size; colour; the hardness and nature of the hydrated alumina precipitated) are affected by the conditions under which they are made; factors such as dilution, temperature and speed of precipitation, and stirring are important and sometimes hard to reproduce. Cochineal is a rich source of dyestuff: its lakes are easier to make from dilute solutions, so it can be difficult to make them on a small scale; our workshop cochineal lakes tended to be very dark in colour and hard to grind, probably for these reasons. The absence of contemporary workshop directions for monitoring the preparations or for the final treatments of the precipitated pigments is not surprising (no manufacturer would publish such commercially sensitive information) but as the stability of the pigments is affected by finishing processes this had to be borne in mind during later experimental work.

Red lake paint reconstructions

In a workshop co-ordinated by the HART project, eleven of the lake pigments (Table 1) were made into a series of linseed oil-based paints, according to a set of criteria to control pigment volume concentration and to avoid cross-contamination (Carlyle and Witlox 2005; see Fig. 1). A set of base paints for each lake was prepared with water-washed linseed oil (LW). Then each base paint was mixed separately with one of the



Fig. 1. Red lake paint making. Photograph K.J. van den Berg.

Table 1. Materials used for making red lakes. Exact numbers, procedures and technical sources: see Kirby (2005) and red lake project archive at ICN.

Name	Preparation of dyestuff	Preparation of pigment ¹
CA	Cochineal insects ground, extracted with citric acid and Na ₂ CO ₃ in water	Dyestuff filtrate, potash alum (aq). Carmine in suspension.
C1	Cochineal insects ground, extracted with water.	Dyestuff filtrate, Al sulphate(aq). K ₂ CO ₃ (aq).
C2	filtrate from carmine preparation	Dyestuff filtrate, cream of tartar, potash alum (aq). Low amount SnCl ₄ and K ₂ CO ₃ (aq).
C3	Cochineal insects ground, extracted with water.	Dyestuff filtrate, SnCl ₄ (aq).
C4	Cochineal insects ground, extracted with water.	Dyestuff filtrate, wheat starch (slurry; aq), SnCl ₄ (aq).
M1	Ground madder, extracted with Na ₂ SO ₄ (aq). Filtered; water washed. Residue into boiling solution of potash alum (aq)	Filtrate + washings, Na ₂ CO ₃ (aq), boil to precipitate pigment.
M2	Powdered madder root, H ₂ SO ₃ (aq); added H ₂ SO ₄ → flakes 'Kopp's purpurin'..	Brown flakes, potash alum (aq), K ₂ CO ₃ (aq).
BM	Ground brazilwood, madder in water	Combined filtrates, Al sulphate, Na ₂ CO ₃ (aq)
B1	Ground brazilwood in water.	Dyestuff filtrate, SnCl ₄ (aq), K ₂ CO ₃ (aq).
B2	Ground brazilwood in water	Dyestuff filtrate, potash alum (aq), K ₂ CO ₃ (aq).
EO	Eosin (tetrabromofluorescein, sodium salt) used as such	Na ₂ CO ₃ (aq), Al sulphate (aq). Eosin, 10 g lead(II) acetate trihydrate (aq).

¹ Laboratory-distilled (aq) used throughout.

All precipitated lakes were washed with (aq) in a Büchner funnel. Washings were checked for residual sulphate or chloride ions (from K alum or SnCl₄) with barium chloride and silver nitrate solutions, respectively. Lakes were filtered, and dried under a stream of dry nitrogen for several days. Potash alum: Aluminium potassium sulphate, AlK(SO₄)₂·12H₂O.

Al sulphate, Al₂(SO₄)₃·18H₂O.

Citric acid: 2-Hydroxy-1,2,3-propanetricarboxylic acid monohydrate, CH₂CO₂H C(OH)(CO₂H)CH₂CO₂H ·H₂O

Cream of tartar: potassium hydrogen tartrate, the mono potassium salt of (+)-2,3,-dihydroxybutanedioic acid, KO₂CCH(OH)CH(OH)CO₂H

SnCl₄: SnCl₄·5H₂O

Lead(II) acetate trihydrate: Pb(CH₃CO₂)₂·3H₂O

following: lead white paint, zinc white paint, megilp, and chalk. Five other sets of paints were prepared, one with lead treated oil (LD) and another one with Paraloid B72, which served as a stable binding medium and inert control. Three remaining sets were prepared with water washed linseed oil (LW) as follows: a fixed mixture of 3 pigments (ultramarine, vermilion, emerald green) plus each lake, a mixture of lake pigments, and a set with the addition of dry powdered wheat starch mixed with the lake prior to grinding. The relative amounts of pigment and additions were calculated according to the density of each pigment. Oil was added during grinding to achieve a base paint that was as stiff as possible while still remaining workable.

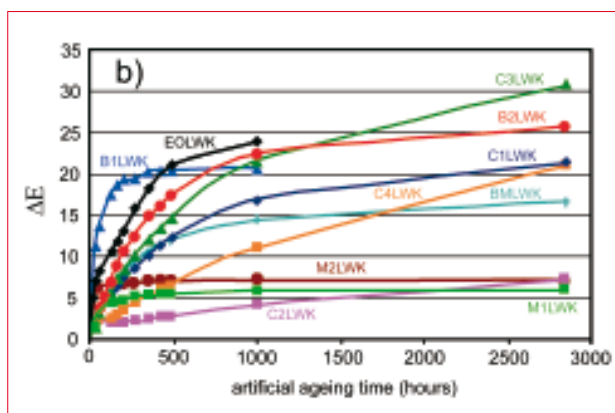
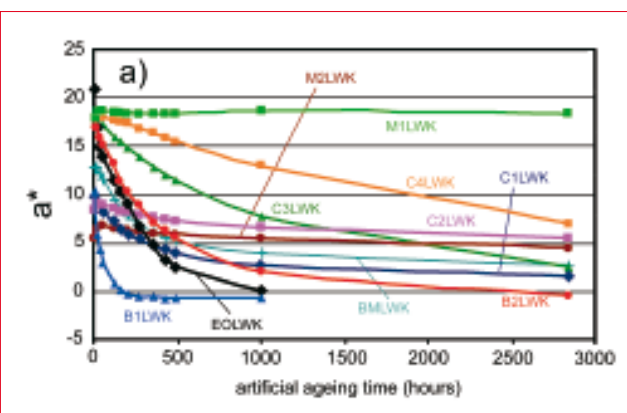
Most dry pigments required grinding in a pestle and mortar prior to use. In general pigments that were easy to grind (in particular madder and eosin) were easy to work into a smooth paint. Hard and glassy pigments (cochineal and brasilwood on tin) gave very gritty, difficult to process paints.

The paints were left to dry for 4 to 5 weeks at low light levels and were touch-dry after this period except for the samples with Megilp (MG) that were still somewhat sticky.

Artificial ageing

Fig. 2 shows the changes in redness [a^* (fig. 2a)] and ΔE values (fig. 2b) during light ageing of the base paints mixed with lead white (LWK). The curves demonstrate the relative stability of madder (M1 and M2) and the cochineal (C1, C2, C3 and C4) samples, in particular those on an aluminium-containing substrate (C1 and C2). The cochineal lakes prepared on tin (C3 and C4) showed poorer light fastness properties. Furthermore, the cochineals on alumina were less stable than madder lakes on the same substrate. Cochineal on alumina alone (C1) was slightly more fugitive than C2, which contains a small amount of tin, further suggesting that the nature of the substrate has an important influence on the light fastness of the paint. Madder (M1)

Fig 2. Colour changes for red lake base paints mixed with lead white paint during light ageing; a) a^* vs time; b) ΔE vs time. B1LWK and EOLWK were not aged past 1000 hrs as they had faded completely by that time. For pigment codes, see table 1. LWK = water-washed linseed oil paint mixed with lead white paint (1/20 w/w).



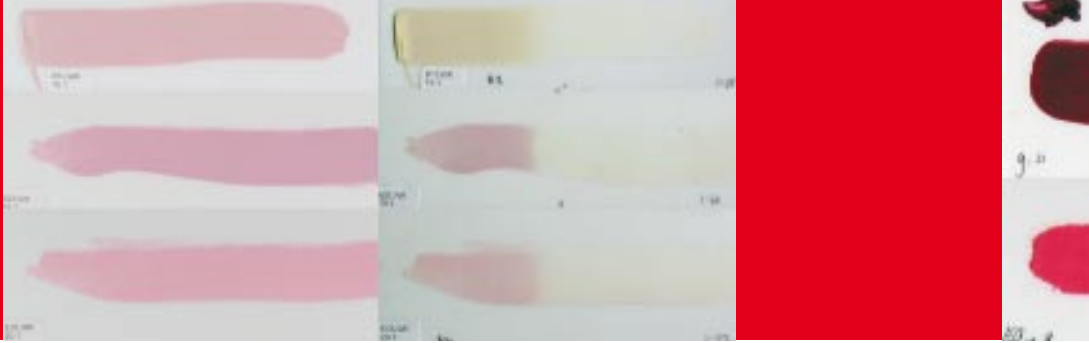


Fig. 3. Colour changes for red lake base paints mixed with lead white paint. a) brasilwood on tin (B1LWK), brasilwood on alum (B2LWK), Eosine lake paints on alum/lead (EOLWK), after 1000 hrs of light ageing calculated equivalent to 17 years under museum conditions. The left side was covered during light ageing. B1 discolours to brown in the dark. Composition of photographs by K.J. van den Berg and L. Carlyle.

was marginally more stable than the lake made from 'Kopp's purpurin' (M2). This may be due to the relatively high amount of alizarin in M1, which is very stable, although its stability relative to that of pseudo-purpurin (in M2) is unclear. The relative instability of eosin (EO), brasilwood (B1, B2) and the brasilwood/madder (BM) combinations compared to the cochineal and madder pigments is evident (fig 2). The brasilwood on tin (B1) discoloured rapidly and was the only pigment which turned brown even in the dark (Fig. 3).

Figure 4 shows the a^* vs b^* curves for several base paints and the mixed lakes in water-washed linseed oil (LW). Clearly, the more fugitive lake generally determines the rate of fading of the mixed lakes. It is striking that the co-precipitate of brasilwood and madder on alum (BM) exhibits the same fading behaviour as the two pigments mixed together (B2M1), even though the pigment size of the latter is much smaller (not shown). During the initial stages of artificial ageing, many lake paints became less yellow because of bleaching of the medium, resulting in a lower value of b^* . This results for the very stable madder lake paint (M1) in a straight vertical line (Figure 4). This effect is not observed in the pigments bound in Paraloid B72 (not shown), whereas the degree of fading of these 'paints' is similar to the normal red lake base paints in oil. The paints that contain brasilwood, however, increase in yellowness (higher value of b^* see fig.

4), due to the formation of yellow intermediates in the fading process (Saunders and Kirby, 1994).

The present results give a good indication of relative stability of the pigments. The addition of starch, chalk or white pigments,

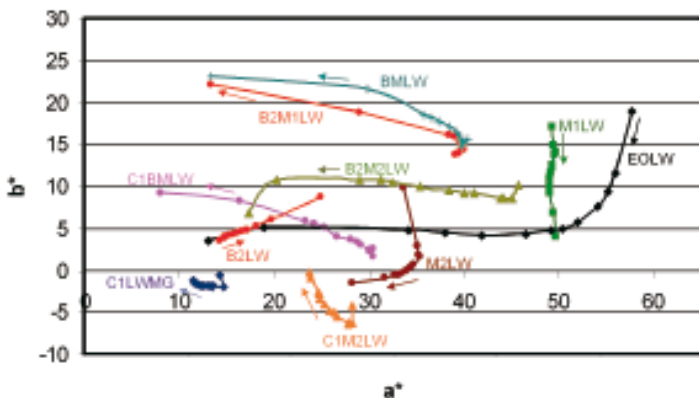


Fig. 4. Colour changes for (mixed) red lake (LW) base paints; b^* vs a^* . Arrows indicate the progress in time. C1LW is presented instead of C1LW which was too dark to give a meaningful result. LW code is not included in the graph. For pigment codes, see table 1.

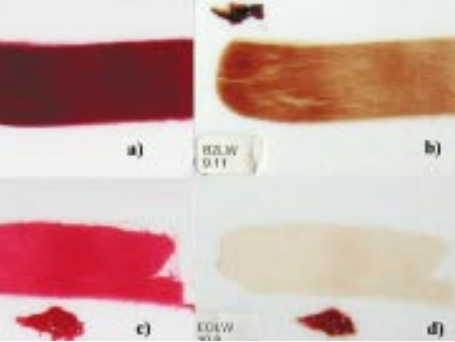


Fig. 5. Influence of thickness in transparent lake paints on fading; a, b) B2LW, before and after ageing; c, d) EOLW, before and after ageing. Composition of photographs K.J. van den Berg.



Fig. 6. Stepwise fading of 10 red lakes paints mixed with lead white paint, showing pronounced fading in all cases except for madder on hydrated alumina (M1). Photograph K.J. van den Berg.

for example, changes the rates of fading somewhat due to concentration effects (see below), but does not influence the fading characteristics of the lake pigment. Comparison of the stability of the resulting paints solely on the basis of the ΔE and a^* (and b^*) vs. time is not entirely valid, as colour changes depend on a number of factors (Saunders and Kirby, 1994). The concentration of the lake plays an important role. The cochineal on alumina paints, for example, were too concentrated to show significant colour change, and their relative stability could only be assessed from samples where the lakes were diluted with additives such as starch, chalk or white pigments. Fading is influenced by transparency and paint layer thickness as well. In thick layers of transparent base paints, colour was retained even in eosin and brasilwood containing paints (Fig. 5), whereas in white-containing paints fading occurred regardless of the thickness of the paint (Fig. 6). This behaviour is explained by the depth of penetration of light; in transparent paint layers light penetrates relatively deeply, the upper part of the paint providing a filter for light of high energetic short wavelength, keeping the red lakes in the lower part intact for a longer time.

In a pilot study, some paint samples were artificially aged under UV filtered light. Another set of samples was light aged under an Argon atmosphere, excluding oxygen. The results showed that in both cases the rate of fading was lower than for samples aged in light with UV present. The UV filtering provided only limited protection; eosin base paint (EOLW) still showed considerable fading after light ageing equivalent to 11 years.

Conclusions

Historical accuracy was somewhat compromised in both lake pigment and paint production, due to a number of factors like the small scale of production and the lack of knowledge about 19th-century paint manufacturing. Nonetheless many similarities were observed between fading and surface degradation phenomena in the reconstructions and those in pictures by van Gogh (Burnstock et al. 2005a).

The relative rates of fading were investigated in a number of different lake paints reconstructed from 19th-century recipes. Cochineal and madder lake paints are more stable than brasilwood/madder combinations, while brasilwood and eosin lakes are the most fugitive. Mixed lakes exhibit a fading behaviour at least initially that is determined by the more fugitive lake. Lakes on a tin substrate are less stable than those on an aluminium-containing substrate. Both densely pigmented and thickly applied paints fade relatively slowly, while all paints faded faster when

mixed with white. Apart from the dilution effect of additions such as lead or zinc white, megilp, chalk and starch, the nature of fading of the pigments does not seem to be influenced. Results of the relative rates of fading of the paints follow the findings of Saunders and Kirby (1994), who examined lakes based on recipes from earlier periods.

The measurements not only illustrate the fugitiveness of a number of lakes which were used by van Gogh, but also demonstrate that his application methods influence to what extent fading has occurred in his paintings, especially when paints are applied thinly or mixed with opaque paints. In the present study, the most fugitive lakes faded in less than 500 hrs of light ageing, which is equivalent to less than 10 years exposure to museum lighting conditions (See Experimental Section – light ageing). This has relevance for the fading and deterioration observed in van Gogh's paintings (Lanfear et al. 2005). It is possible that his redwood and eosin-containing paints may have faded during or soon after his short life. Under uncontrolled lighting conditions (outside a museum), fading and colour shifts are likely to have occurred even more rapidly.

Acknowledgements

Stichting Restauratie Atelier Limburg is acknowledged for access to its artificial ageing facilities. Muriel Geldof and Maarten van Bommel assisted in the organisation of the workshop. David Saunders, Arie Wallert and Luuk van der Loeff participated in the first workshop and are thanked for valuable discussions. Ester Ferreira and Jaap Boon are acknowledged for editorial support.

References

- Burnstock A., Lanfear I., van den Berg K.J., Carlyle L., Hendriks E., Kirby J. (2005a). *A comparison of the fading and surface deterioration of red lake pigments in six paintings by Vincent van Gogh with artificially aged paint reconstructions*. In: *Proceedings of the 14th Triennial Meeting of the ICOM Committee for Conservation Meeting in Den Haag* (I. Vergier ed), Preprint book I, James and James, London. p. 459-466.
- Burnstock A., van den Berg K.J., House J. (2005b). *Painting techniques of Pierre-Auguste Renoir: 1868-1919*. *ArtMatters* 3, Waanders, Zwolle. p 47-65.
- Carlyle L., Witlox M. (2005). *Historically Accurate Oil Paint Reconstructions*. In: *Art of the Past - Sources and Reconstructions* (Clarke, M., Stijnman A., Townsend J.H. eds.) Archetype Publications Ltd., London. p. 53-59.
- Hendriks E., van Tilborgh L. (2001). *Van Gogh's 'Garden of the Asylum'; genuine or fake?* *The Burlington Magazine*, 145-156.
- Kirby J., Stonor K., Burnstock A., Roy A., Grout A., White R. (2003). *Georges Seurat's Painting Practice: Theory, Development and Technology*, *National Gallery Technical Bulletin* 24, 4-37.
- Kirby J. (2005). *Reconstructions of French 19th-century red lake pigments for the Red Lake Project*. In: *Art of the Past - Sources and Reconstructions* (M. Clarke, A. Stijnman, J.H. Townsend eds.) Archetype Publications Ltd., London, p. 69-77.
- Saunders D., Kirby J. (1994). *Light-induced colour changes in red and yellow lake pigments*, *National Gallery Technical Bulletin* 15, 75-97.
- Van Bommel M., Geldof M., Hendriks E. (2005). *Examination of the use of organic red pigments in paintings by Vincent van Gogh (November 1885 to February 1888)*. *ArtMatters* 3, p. 111-137.

Multidisciplinary research on the paintings ensemble in the Oranjezaal of the Royal Palace Huis ten Bosch

COMPARATIVE STUDIES OF THE PAINTINGS IN THE ORANJEZAAL

Abstract

The painted decorations in the Oranjezaal of the Palace Huis ten Bosch in The Hague, were commissioned by the architect Jacob van Campen and executed between 1648 and 1652 by twelve prominent painters of the northern and southern provinces. The Oranjezaal, made in memory of stadholder Frederik Hendrik, remained very much intact over the centuries and minor interventions could be dated through archival research. During the restoration from 1998 to 2001 under the supervision of the Limburg Conservation Institute, extensive interdisciplinary research was done into the painting technique and the history of restoration. Art historical research would lead to a new and innovative interpretation of this unique ensemble. Comparative analysis of pigments and binding media analysed gave insight into the material choices and their working methods of the painters and the changes of the paints due to aging. The different varnishes were identified and dated. The influence of solvents on the molecular structure of the original paint layers was examined within the reality of ongoing restoration procedures. In an extensive interdisciplinary effort, the findings will be published in 2007 by the Netherlands Institute for Art History (RKD) and the State Building Department in The Hague.

¹ SRAL Stichting Restauratie Atelier Limburg, Avenue Ceramique 224, 6221 KZ, Maastricht



Introduction

The conservation of the Oranjezaal in the Huis ten Bosch Palace in The Hague was commissioned by the State Building Department in January 1998 and completed in June 2001. An extensive preliminary investigation was carried out between February and August 1997 to answer vital questions relating to the treatment proposal. Multidisciplinary investigations were pursued during the whole period of the treatment and research was carried out on paint and varnish samples up until 2006. The quite extraordinary coincidence in time between the NWO Programmes of MOLART (1995-2000) and NWO de Mayerne (2000-2006) and the Oranjezaal project (1998-2001), created the opportunity to solve certain relevant and urgent questions in relation to the treatment and at the same time to develop broader lines of art technical and art historical investigation. Scientific research carried out within the reality of the field of cultural heritage is rewarding in equal proportion to the trouble it takes. The "privileged moment" of restoration for undertaking this type of interdisciplinary research was aptly defined by Paul Coremans in 1953. It is still very true today.

The organisation of the project Oranjezaal tended at times to be complex due to the diversity of institutional idiosyncrasies. The Oranjezaal itself became temporarily a delicate "building site" at the centre of the private home of the Royal family. Research was carried out in various institutions such as the Royal archives, the RKD in The Hague, the ICN and FOM/AMOLF in Amsterdam. At the same time, the team of conservators was dealing with architects, technicians and civil servants very much concerned with functionality and technical issues. On the other hand and in a very pragmatic manner, budgets for research could be added up once a common ground was found. Funds coming from the State Building Department, the State Agency for Monuments, NWO, SRAL, RKD and private funding, were available over a long period of time. The result of all this research will be presented in the final publication in 2007 under supervision of the RKD in the Hague.

Combining conservation projects with applied scientific research in the post-academic training programme for conservators has been the main objective of the Limburg Conservation Institute (SRAL) for the past fifteen years. The SRAL students, having all completed a degree in art history, architecture or chemistry before starting their training in conservation, were fully equipped to participate actively into the research programme of the Oranjezaal. Technical art history or the investigation into the making process of the paintings and conservation science geared towards answering questions in relation to the treatment, were continuously integrated into the practice



of restoration. Scientists from FOM/AMOLF or ICN worked with the students in the same environment, asking questions and defining paths to find answers. Young scientists on a PhD track were part of the team, bringing their knowledge and expertise and

finding in the Oranjezaal answers to some of their questions. The dynamic effect of these complementary activities was very effective, as the scientific harvest will show.

The Oranjezaal, a privileged space for historic and art technological research

The commission for the Huis ten Bosch Palace was given to the architect Pieter Post by the Stadhouder Frederik Hendrik in 1647. It was intended as a country dwelling in the Palladian tradition for his wife Amalia van Solms. After his death in 1648, the iconography of the central hall was converted to represent a mausoleum by his widow. She asked the famous architect Jacob van Campen for the design. Between 1648 and 1652, twelve prominent artists from the Northern and the Southern Provinces created an ensemble of 43 paintings on canvas and on wood, blending their work into the architecture to form a *trompe l'oeil* triumphal procession in memory of Frederik Hendrik, according to the classicist tradition found in Roman Antiquity. Regarding the ensemble commissioned to the twelve artists, the first consideration during the conservation project was to maintain or reconstruct van Campen's original intention of the architectural uniformity of the building structure, available light and the representation on the canvas and wooden supports in the Oranjezaal. Exposure of the art to climatic circumstances and the history of interventions were similar and well defined. This created ideal circumstances to compare the variables *in casu*, the painting techniques, the various materials, the execution and the reaction of the paintings to natural ageing and past conservation treatments. However, foremost, it was the degree of authenticity of the Oranjezaal ensemble that was remarkable, as it remained intact over the centuries although minor interventions and adaptation to changing taste were carried out. These changes could be dated in the archives and this information provided in its turn, a solid historic framework for the paint research of the pictures. Art historical research had concentrated in the past on iconographic



and historic issues and of course, the architecture of the building had been studied extensively. Little was known however about the actual painting technique of the twelve artists concerned and above all, no clear concept of the ensemble could have been deduced because of the material condition of the painted surfaces and the lack of art technical information.

Questions raised by the treatment proposal

The State Building Department, following a first investigation in 1986, commissioned the SRAL in 1996 to undertake a new programme of research aiming at a treatment proposal that could be submitted to the steering group of the project. Research into the history of restoration, stratigraphic examination of the finishes in the architecture, technical examination of the paintings and cleaning trials were undertaken and presented in a preliminary report. The main conclusions of this report can be summarised as follows:

- a. The treatment should aim at going back to the authentic surfaces of the original elements of the Oranjezaal by removal of later additions such as altered varnishes and overpaints.
- b. In view of the large proportion of authentic materials and structures, minimal interventions in terms of conservation should be pursued.
- c. The changes in form due to altered functionality of the ensemble such as the windows to the garden and the door replacing the chimney piece in the western wall, should be kept intact.
- d. Climate control and general measures of preventive conservation should be implemented.
- e. Careful monitoring of the ensemble in the years after the treatment should be allowed for.

The excellent overall condition of the paintings on canvas and on wood justified clearly the restrained and minimalist approach towards conservation measures. The large majority of all the canvases had never been lined and were still stretched with strings in the fashion of the seventeenth century. The priming of the paintings could be dated and attributed to the "primuorder" Frans Oliviers. It was analysed as being lead white and raw umber bound in oil over an isolating layer of the linen fibres with animal glue. Adhesion of the paint layers was generally excellent. Facing the varnish removal of large surfaces of non-lined paintings from the mid 17th century, it seemed imperative at the time of the preliminary investigation to re-think the procedures, the methods and aesthetic aims of the intervention. Choices had to be made in terms of levels of cleaning and its methodology. It was imperative to investigate the effect of cleaning on the perception of the ensemble. Originally, the relation between paintings on canvas below the cornice and those on wood in the vaults had once been coherent in the rendering of space. The eye could forget the different structure of the support and move upwards towards the sky, following the spatial illusion created by the visual concept. How the various painters had accomplished this required a thorough examination of their painting technique and their choice of materials. Ageing had treated both regions differently. The canvases, on their original stretchers, were rather even and a slight sagging did not prevent the reading of the composition whereas the planks in the vaults had shrunk, creating a horizontal pattern of shadow lines. The surfaces in both areas were covered by a shiny layer of yellow varnish. This varnish layer reflected the light coming from the windows and masked the painted surface in its rendering of space. In a similar way as a glass window will hide the room behind it when the depth and shadow are overpowered by light. In the perception of the painted surface, the paintings in the vault looked older because of the slight distortion of the planks and the shadows of the open seams. Would a total cleaning affect both surfaces differently and what would be the consequences in terms of spatial perception? Would an even layer of yellow varnish maintained locally in its function of patina be beneficial to the lecture of the irretrievably aged ensemble? One could argue that the distorted surface of the support would validate a certain "patina", a yellowed surface that our brain reads as "aged". On the other hand, the removal of shiny and yellow varnish, would give a maximum chance to the paint itself, the vehicle of colours and depth in composition. Cleaning trials and their documentation with UV fluorescence were made first in the vault to evaluate the change in colours and the perception of space and subsequently on the canvases to match the effect. In situ work was supported by multidisciplinary advice from various

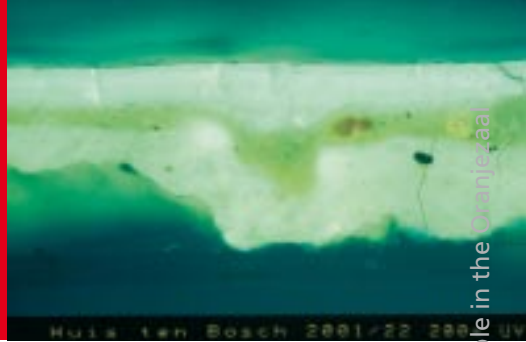


experts and further research to make informed decisions.

First, the material history of the paintings had to be retraced in the archives and material evidence of various interventions had to be recognised on the paintings. The archival research was done by Paula van der Heijden while Mireille te Marvelde conducted the examination of the paintings. Secondly, the chemical nature of the original binding media, pigments and dyestuffs was thoroughly analysed involving the examination of more than five hundred paint cross-sections and the examination of hundreds of separate samples. This work was coordinated by Lidwien Speleers, while Annelies van Loon was in charge of the chemical investigation of the paint cross-sections. The nature and chemistry of the different varnishes were analysed by Gisela van der Doelen as part of her PhD thesis work while the application of different varnish layers was dated using archival sources studied by Mireille te Marvelde. Thirdly, the consequences of varnish removal in terms of molecular structure of the original paint layers had to be assessed involving a thorough examination of the nature of the original binding media under supervision of Jaap Boon and his team involving Gisela van der Doelen, Jorrit van den Berg, Ester Ferreira and Katrien Keune at AMOLF. Research into the interaction between different solvent mixtures and techniques of application with the original binding media, was carried out by Ken Sutherland as part of his PhD work. Finally, the study of the painting technique served the unique purpose of understanding the genesis of the ensemble in terms of the rendering of light. This was the task of Lidwien Speleers who studied the painting materials and their application and Margriet van Eikema Hommes who studied contemporary sources and found evidence of their implementation of this information in the painting technique, varying according to the iconography and according to the particular setting of the paintings in the room itself. The scientific and art technical research took, understandably, much longer than the time schedule could accommodate. After preliminary research results were available, a protocol for treatment and cleaning was developed that involved a preliminary consolidation of the paint layers with a gelatine solution and solvent application in gel form to avoid migration of the solvents into the porous structure of the canvas

The organisation of the Oranjezaal research project

During the course of restoration, many observations were made and discussed within the multidisciplinary setting of the project. Many questions on materials used came up before and during treatment and were further pursued in the collaborating research laboratories. After completion of the restoration in 2001, the access to the



Oranjezaal was restricted to short bi-annual control sessions and the scientific team was dispersed over different institutions, still working together but in dislocation. The documentation was brought to the RKD and the paint samples were located at AMOLF. This fragmentation and the impossibility to verify in situ visual hypotheses on a daily basis, certainly slowed down the multidisciplinary research process. This reality and the important amount of data emerging from the project explain without doubt the postponing of the final RKD publication towards the end of 2007. The funding of additional time for research, editing and publication was, as in many similar cases, difficult to find once the restoration project was completed. The generous contribution of various institutions housing the “post-Oranjezaal” team, such as the RKD, the ICN, AMOLF and SRAL, kept the project “alive” and the NWO programmes of de Mayerne certainly added the scientific depth in terms of sophisticated analytical resources. It is this combination of creativity and “bonne volonté” that will be remembered.

The material history of the paintings in the Oranjezaal

Wax lining

The preliminary investigation had shown that historical data from the archives could be traced back to the material evidence on the paintings. The lining of a few paintings could be identified as being by the hand of conservators from the 18th and 19th century. The dating by Mireille te Marvelde of the earliest known wax lining in Europe (Nicolaas Hopman in 1806) and the identification of the lining mixture (colophony and beeswax) by the MOLART team at AMOLF is exemplary for the multidisciplinary approach during the de Mayerne programme. The results of this combined research were necessary to make choices during treatment but they could also be slotted into broader programmes of investigation. Mireille te Marvelde included her findings in the Oranjezaal into the national context of the study of the history of restoration in the Netherlands (Te Marvelde 1999) and in the international context by her contribution to the history of wax-lining in Europe. (Te Marvelde 2001; 2002 and in preparation)

Varnish

The study of the varnishes was for similar reasons, essential within the discussion about cleaning and varnish removal provided arguments for the definition of their “final appearance” in terms of degree of saturation of the final varnish layers. It could be clearly demonstrated that the “original appearance” of the paintings had



been saturated but indeed not shiny. The concept of “peinture matte”, unvarnished or lightly saturated oil paint, fitted perfectly into the spatial concept of the Oranjezaal and its *trompe l'oeil* effect. The early confrontation of evidence coming from UV fluorescence of different residual layers of varnish identified by stratigraphic examination and dated through archival research, was essential for decision making during treatment. An outstanding example is the identification of islands of the oldest dated varnish (Jan van Dijk, 1767) with its typical strong yellow fluorescence (diterpenoid resin, identified by Gisela van der Doelen) still preserved on the red glazes added to the vermillion underpainting in a painting by Pieter de Grebber. Subsequent cleaning by Hopman in 1806 partially removed this varnish and maybe parts of the red glazes. The vermillion in the highlight had altered due to the now unfiltered light exposure and the presence of chlorides in the vermillion. Katrien Keune and Boon (2005) identified the alteration products of the vermillion (red mercury sulphide, HgS) that changed into a black alteration product with elementary mercury nano-particles [$\text{Hg}(0)$] towards grey and white end products of mercuric chloride (HgCl_2).

Dyes in glazes

The dyestuff in the red glazes was analysed by Marc Clarke et al. (in press) in a close collaboration between the ICN, the University of Antwerp and the Royal Institute for Cultural Heritage in Brussels. A broad choice of paint samples covering almost every painter in the Oranjezaal could be analysed by HPLC, revealing a constant presence of cochineal along with many mixtures. The presence of tannin suggested that the dyestuffs were made by recycling dyed textiles. The inorganic substrates were analysed by TEM and aluminium- containing particles were a constant marker in the different glazes. The very relevant question about differences in painting materials used by the painters in the Oranjezaal and the vital question about North/South



Netherlandish differences in approach could not be answered because of the variety in inorganic substrates, additives or residues of the making process, and the constant presence of cochineal. This negative answer in terms of regional differences, could bring us a step further in the research into paint trading and commercial contacts, an old area of interdisciplinary research deserving a further input.

Swab removal of fatty acids

Following a similar thread as the "*Solvent extractable components of oil paint films*", a topic in the PhD research done by Ken Sutherland (2001) concerning the Oranjezaal, it was shown that very small or non-measurable quantities could be detected in the cotton swabs after varnish removal. However, varying quantities of leachable materials could be detected by Gas Chromatography in the samples before treatment. The measuring of "real" cleaning trials as opposed to former "immersion" trials of the paint samples was a significant step further in terms of scientific objectivity applied to restoration procedures. An interesting exception was the amount of extracted fatty acids from a mechanically cleaned area of vermilion paint from a painting by Soutman. In this particular case, painting technique, history of restoration and degradation phenomena came in very close contact indeed. Knowledge about "danger areas" in the painted surface and their identification before treatment is essential for further development of our knowledge about the effects of cleaning procedures on the molecular structure of the binding medium. It is essential for predicting unwanted acceleration of degradation phenomena caused by solvent cleaning.

The binding media

An extensive survey of the binding media in a group of twelve paintings by eight different artists from the Oranjezaal was presented at the ICOM-CC conference in the

Hague in 2005 by Ferreira, van der Horst and Boon (2005), complementing the studies done in the MOLART programme by Jorrit van den Berg (unpublished reports and 2002). Their findings were consistent with “those from studies of other paintings from the same period and geographical origin with exception of the lack of conventional pre-polymerization”. The analyses were made in zones of lead white chosen for their good drying properties of linseed oil and in dark areas, known for their poor drying properties. Linseed oil was the main component and “the degree of light ageing was reported to affect the amount of suberic acid, implying that the azelaic : suberic ratio is affected by the history of the painting. Therefore the interpretation of this ratio should be cautious, especially when the history of the paintings is unknown”. An interesting conclusion indeed if one takes into account the orientation of the room and the amount of sunlight coming in through the southern windows, affecting certain colour zones more than others

Pigment ageing

In a paper presented at the IIC conference in Munich by Annelies van Loon et al. (2006), the results of the examination of nearly 500 paint cross-sections were reported. This remarkable amount of work, made possible with support of FOM and de Mayerne Programmes, illustrates how important a quantitative approach can be for the ultimate interpretation of stylistic characteristics of 17th century paintings. The work shows that degrees of change due to ageing can be related to the quality of the pigment, the influence of the binding medium and the ways that painters applied their materials. In the relation to the painting technique it became clear for example, how certain known paint defects could be counteracted by the painters, using specific antidote measures while un-known ageing properties, obviously, were not counteracted at all. This analytical research also gives us the instrument to judge the long lost “original state of the painting”, enabling us ultimately to appreciate the intended stylistic balance between the different colour zones, information essential for an adequate interpretation of the painting style of the artists.

The stylistic and art historical interpretation of the painted decorations in the Oranjezaal

Working gradually towards a clear description of the original visual concept of the Oranjezaal, the close collaboration between Lidwien Speleers and Margriet van Eikema Hommes within the De Mayerne Programme has been extremely fertile. The publication of the essay about the visual concept in the Oranjezaal Book in 2007 will be the actual end product of almost nine years of interdisciplinary work, bringing together and integrating the results of extensive technical paint research and art historical interpretation (see Ekkart 2007).

This essay will combine former publications by the two authors such as their contributions in Art Matters 3 about the “Regulen” by de Grebber, the “rules” for painting and rendering of volume within pictorial space and the actual analysis of the different painting techniques (Van Eikema Hommes 2005a, b). It could be proven that painters varied their methods in relation to the iconography and adapted their technique according to the setting within the architecture.

The general scheme of this essay dated 25 April 2006 is given here in translation :

1 The visual concept of the Oranjezaal

- 1.1 The "Regulen" by Pieter de Grebber (1649) (see Margriet van Eikema Hommes, 2005 a)
- 1.2 An extraordinary light concept in the 17th century. The rendering of light in the painted decoration of the Oranjezaal in the Huis ten Bosch Palace (see forthcoming publication by Margriet van Eikema Hommes)
- 1.3 The role of the architect Jacob van Campen
- 1.4 Selection of the painters
- 1.5 A comparison with other ensembles (Rubens, the architecture of Pompa Triumphalis...)

2 The coordination and the implementation of the visual concept

- 2.1 The sketches by different painters and the plans of Jacob van Campen
- 2.2 The portraits of Frederik Hendrik and other members of the family, their reproduction and representation
- 2.3 The trompe l'oeil architecture in the paintings of the triumphal cortege, their various degrees of completion and the reason why
- 2.4 The work in situ

3 The Painters at work

- 3.1 An introduction about painting practice in the 17th century
- 3.2 A description of the painting technique of the twelve Oranjezaal painters (see publication of Margriet van Eikema Hommes & Lidwien Speleers, 2005)
- 3.3 Discussion of the results: the preliminary drawing, underpaint, last touches and the workshop practice
- 3.4 A comparison between the painters from the northern and southern provinces

4 Technical data

- 4.1 The canvases and their priming, in collaboration with Michiel Franken, RKD
- 4.2 Pigments, binding media, metal leaf

Acknowledgements

My deepest gratitude goes to the multidisciplinary team of the Oranjezaal and to institutions such as NWO, RGD, ICN, RKD, RDMZ and the Gravin van Bylandt Stichting who funded the restoration and research. Many thanks to the SRAL team for the efficiency and creativity in coordinating the project.

Prof. Dr. Jaap Boon has been a constant bridge between disciplines in the Oranjezaal Project. I would like to thank him for that and the editorial revision of the text. Kate Seymour was, as ever, a great help for checking my English.

References

- M. Clarke, P. Fredrickx, L. Speleers, I. Vanden Berghe, and J. Wouters (in press), *Comparative studies of seventeenth-century Netherlandish red lake glazes in the Oranjezaal, Palace Huis ten Bosch*. In: DHA 22 (a conference held in Riggisberg)
- Ekkart R. (editor) with contributions by Lidwien Speleers, Margriet van Eikema Hommes, Michiel Franken, Mireille te Marvelde, Anne van Grevenstein, et al. (2007) *The Oranjezaal, to be published in 2007*.
- Ferreira E.S.B., Van der Horst J., Boon J.J. (2005), *Chemical aspects of the binding media of the Oranjezaal ensemble: an insight into 17th century Netherlandish materials and methods*. In: *Proceedings of the 14th ICOM-CC meeting in The Hague* (I. Vergier ed), Preprint vol.II, p.774-782.
- Keune K, Boon J. J. (2005). *Analytical imaging studies clarifying the process of the darkening of vermilion in paintings*, *Analytical Chemistry*, p. 4742-4750.
- Sutherland K.N. (2001). *Solvent extractable components of oil paint films*, PhD dissertation University of Amsterdam. Report of MOLART Series: MOLART 3. See chapter 6: "Measurements of cleaning effects on paintings", p117-138.
- Te Marvelde M., Speleers L.B.J., Van der Doelen G. (2002) *Research into the conservation-restoration history of the paintings in the Oranjezaal*, In: *Mol-Art, Final report and highlights, 1995-2002*, (M. Clarke and J.J.Boon eds), AMOLF, Amsterdam.
- Te Marvelde, M. (1999). *Research into the history of conservation-restoration: Remarks on relevance and method*. In: *Processings of the ICOM-CC meeting in Lyon* (R.Vontobel ed), vol 1, pp194-199
- Te Marvelde, M. (2001). *How Dutch is "The Dutch method"? A History of Wax-Resin Lining in it's International Context*. In: *Past Practice-Future Prospects, The British Museum Occasional Paper nr 145*, (Andrew Oddy and Sandra Smith eds), p.143-149
- Te Marvelde, M. (in preparation), *Chapter about wax-resin relinings*. In *The Butterworth's Series about conservation of paintings* (Joyce Hill Stoner ed). To be published in 2008.
- Van den Berg, J.D.J. (2002). *Analytical chemical studies on traditional linseed oil paints*. PhD dissertation University of Amsterdam. Report of MOLART Series: MOLART 6
- Van Eikema Hommes M. (2004). *The Contours in the Paintings of the Oranjezaal, Huis ten Bosch*. In: *The learned eye. Regarding Art, Theory and the Artist's Reputation, Essays for Ernst van de Wetering*, Amsterdam University Press, p.58-84.
- Van Eikema Hommes M. (2005a). *Pieter de Grebber and the Oranjezaal in Huis ten Bosch, Part I: the Regulen (1649)*, *Art Matters* 3, p.20-36.
- Van Eikema Hommes M., Speleers L.B.J. (2005b). *Pieter de Grebber and the Oranjezaal in Huis ten Bosch, Part II: variations in painting technique*, *Art Matters* 3, p.37-46.
- Van Eikema Hommes, M. H. (forthcoming). *A remarkable seventeenth-century light concept: The rendering of light in the paintings in the Oranjezaal, Huis ten Bosch*. In preparation.
- Van Loon A., Speleers L.B.J., Ferreira E.S.B., Keune K., Boon J. J. (2006). *The relationship between the degree of preservation and painting technique in the Oranjezaal ensemble, Huis ten Bosch Palace*. In: *The Object in Context: Crossing Conservation Boundaries* (D. Saunders et al. eds), IIC, London, p. 218-223

Recipe databases for historical oil painting materials: Winsor & Newton Archive

RECIPE DATABASES FOR HISTORICAL OIL PAINTING MATERIALS

Abstract

The nineteenth-century archive of commercial recipes for artists' materials from the English colourmen Winsor & Newton has been digitally imaged and indexed in an innovative database. The archive, beginning in the 1830s, details the manufacture of pigments, binders, mediums and the preparation of tube paint, thereby providing access for the first time to commercial 19th century paint formulations as well as insight into the relationship between the artist and his materials. This unique resource is invaluable for authenticity studies, scientific analyses and the care and preservation of historic works of art. A new method for developing text-based databases based on manuscripts was developed which eliminates interpretation and transcription errors. This database will have a lasting impact on the study of art technology worldwide.

¹ Hamilton Kerr Institute, Mill Lane, Whittlesford, Cambridge, CB2 4NE, England, mcc30@cam.ac.uk

² Tate Britain, Millbank, London, SW1P 4RG, England, leslie.carlyle@tate.org.uk

Fig. 1. Painted out samples (Winsor & Newton manuscript "Moist Tubes 469 x 839" (c.1880), page 603b.

Introduction: the material

The Winsor & Newton colourmakers and artists' suppliers archive consists of hand-written recipe books, process records and shop floor accounts (product manufacturing timing and costs), as well as miscellaneous details of their daily operations from the beginning of their company in the early 1830s through to the twentieth century. This is the first time the full depth of the archive has been made available to researchers outside the Winsor & Newton Company.

It covers detailed information on the manufacture of pigments, binders, mediums and the preparation of tube paint, thereby providing a unique insight into nineteenth century painters' materials along with factory-floor practices of a major nineteenth-century artists' pigment and paint manufacturer. Working notes accompanying recipes and procedures show how (and when) processes were revised to improve quality, reduce expense, or take account of variability in raw materials. Often painted-out samples of experimental formulations are included (Figure 1). Calculations for labour and equipment throughout provide costing information, so the commercial value of a given material can be closely evaluated.

To date no other comprehensive historical archive of detailed recipes for making artists' oil paint, watercolours and other materials, is known. The value of the Winsor & Newton recipe books, is that they allow researchers to determine what materials were used to create a given pigment, colour mixture, or tube paint: essential information for interpreting analytical data from actual paintings in authenticity studies and evaluations of deterioration. To establish whether an artist mixed a given set of pigments to achieve a colour, or added certain materials to their paint, or whether this was already done by the paint supplier is significant in understanding the artist's choices and individual relationship to his materials. Furthermore, paint defects, such as the powdering of lead chromate pigments in important works of art can be better understood and treated by studying contemporary recipes for this material.

During the De Mayerne project attention was focussed on the part of the archive specifically dealing with oil painting materials (10942 pages containing 9339 recipes, from a total archive of 17006 pages).

The Database project

A new database approach has been developed for making the contents of each manuscript easily accessible without the need for exhaustive transcription or complex editing. The database displays full images of each hand-written page from the archive



alongside an electronic index and summary of individual recipe contents. This removes the problems of full-text entry, and allows the rapid generation of indices. Since the original page is always visible to the user, subsequent researchers need not be restricted to interpretations made by the individuals creating the database. Fresh interpretations of the content of the text can continue, unlike conventional publications or databases where the information is necessarily filtered through the original editors.

The database fields include subject classifications and a summary of the information from each recipe. Researchers can search for specific recipes, or for specific materials. Chronological and alphabetical sorts are of course integral to the search functions. To facilitate searches in detailed records, all materials mentioned in a given recipe or manufacturing description are entered, using both the original wording and an interpreted description of the material to clarify obsolete words, difficult words, code words or abbreviations (e.g. "muriatic acid" = hydrochloric acid). Throughout the archive abbreviations have been used frequently with the original meaning often appearing in only one location. Therefore the full interpretation of an abbreviation would be extremely difficult to access without an electronic database. In detailed records, recipes are also indexed by quantities and proportions of materials, to enable variations or similarities in preparation to be identified. British measures are displayed side by side with SI units.

Example of use: Corot's tube paints

The information on painting materials yielded by the archive will be an invaluable resource for investigations into nineteenth century materials and techniques. If an unexpected compound or element is noted during analysis of a paint sample, possible explanations for its presence may be found in the archive database. Undated tubes of

Fig. 2. Complex layers of text, demonstrating the advantages of using Page-Images instead of transcriptions in the database. (Winsor & Newton manuscript "C.M.P. 01", (1835-1836), page 56.)

paint in a paint-box that belonged to Corot (1796–1875) were analysed by Hermens *et al.* (2002). A partly legible label from Winsor & Newton read 'Roman...'. The authors speculated that this might be Roman Ochre, but were puzzled because: 'We found, however, both yellow ochre and a small amount of chrome yellow...'. The Winsor & Newton database was searched for 'Roman' plus 'chrome'. This located 12 recipes including two, dated before 1854, for 'Roman Ochre in Oil. (Artists)'. Both consisted of Roman Ochre and Raw Sienna in poppy oil, with the addition of 3 per cent of Deep Chrome. This confirms the identification of the label as appropriate for Roman Ochre and accounts for the presence of chrome yellow. The attribution of the tube to Corot himself is possible as the recipe's date (circa 1854) falls within his lifetime.

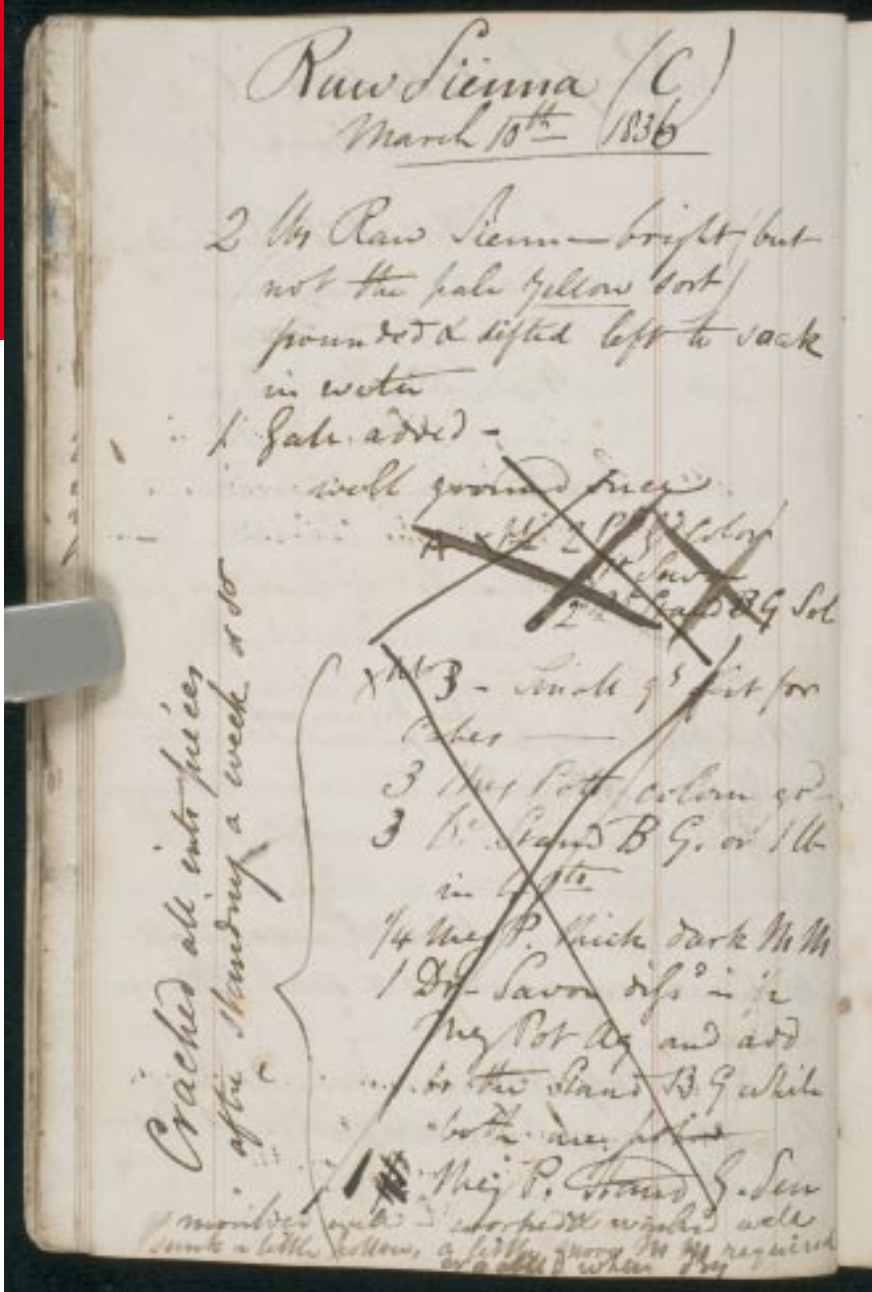
Future developments

NWO's funding of this project was successful in demonstrating to the Arts and Humanities Research Council (a U.K. research funding body) the importance of continuing support for the archive's accessibility. The success of the NWO-funded project convinced the AHRC to fund the project for a further two years. This will expand the range and depth of information indexed, to include Winsor & Newton's substantial collection of watercolour recipes. It will also allow further photography at higher quality and eventual publication. This work will be hosted by the Hamilton Kerr Institute of the University of Cambridge's Fitzwilliam Museum. Recognising the fundamental contribution this archive will make to the study of artists' materials and techniques, the Tate gallery in London are particularly anxious to contribute expertise and resources to the database's development and support.

During 2006, the database will be deposited at Rijksbureau voor Kunsthistorische Documentatie in Den Haag. RKD will ensure the future storage and accessibility of this material. During 2006-7 the database will be hosted at the Hamilton Kerr Institute, where it will be enlarged and enhanced. When this is completed then copies of all data files and images will be deposited at the RKD, at the University of Cambridge, and at the UK Arts and Humanities Data Service, at Winsor & Newton, and at the Tate Hyman Kreitman Research Centre London, thus ensuring a distributed, safe, secure, and sustainable future.

Conclusions

The Page-Image database concept has been shown to be excellently suited to the purpose of making rare or unique historic archives widely available and easily



accessible. The use of electronic images of each manuscript page ensures that indexing is faster than transcribing full texts, especially when the texts are hard to read. This is vital in making such a large archive available quickly and comprehensively. Using images from the original document means that all diagrams, annotations, corrections or deletions other hands are also available, (Figure 2) and, importantly, it allows readers to use their own experience to read passages that might be incomprehensible to the first compilers of the database.

This database will facilitate the interpretation of analytical results and their correlation with information from other documentary sources, and so will be of great

interest to conservators, conservation scientists and art historians. As an important product of the De Mayerne Programme, this database will have a lasting impact on the study of art technology.

Acknowledgements

We would like to warmly thank Colart, the parent company of Winsor & Newton for all their support, encouragement, and assistance, especially Emma Pearce, Ian Garrett, Alun Foster and Sarah Miller. Winsor & Newton do not have a mandate, nor is it in their particular interest, to develop a database of their private archive, and so we are all extremely grateful to them for making this material available, and for their continuing help and enthusiastic support. We are indebted to Bas van Velzen for building the draft version of the database, and to Maartje Witlox for programming advice. We would like to thank the ICN for hosting this project and the Stichting Restauratie Atelier Limburg for administrative support.

Reference

- Hermens E., Kwakernaak A., van der Berg K-J., Geldof M. (2002). *A travel experience: the Corot Painting Box: Matthijs Maris and 19th century tube paints*, *Art Matters* 1, 104–121.

Appendixes

Theses
in the period 2002-2006

List of publications
in the period 2002-2006

List of presentations
in the period 2002-2006

Theses in the period 2002-2006

PhD theses supported by MOLART or the De Mayerne Programme

Van den Berg J.D.J. (2002). Analytical chemical studies on traditional linseed oil paints. PhD dissertation University of Amsterdam. Report of MOLART Series: MOLART 6

Van der Weerd J. (2002) Microspectroscopic Analysis of Traditional Oil Paint. PhD dissertation University of Amsterdam. p. 182. Report of MOLART Series: MOLART 7

Wyplosz N. (2003) Laser desorption mass spectrometric studies of artists' organic pigments. 2003, PhD dissertation University of Amsterdam. Report of MOLART Series: MOLART 8

Languri G.M. (2004) Molecular studies of asphalt, mummy and Kassel earth pigments: characterisation, identification and effect on the drying of traditional oil paint, PhD dissertation University of Amsterdam. Report of MOLART Series: MOLART 9

Keune K. (2005) Binding medium, pigments and metal soaps characterised and localised in paint cross-sections, PhD dissertation University of Amsterdam. p. 181. Report of MOLART Series: MOLART11

Marino B. (2006). Paints quantified: Image analytical studies of preparatory grounds used by Van Gogh, PhD dissertation University of Amsterdam.

Hendriks E., Van Tilborgh L. (2006). New Views on Van Gogh's Development in Antwerp and Paris; an integrated art historical and technical study of his paintings in the Van Gogh Museum. PhD dissertation University of Amsterdam

Research for PhD dissertations or Master theses supported by the MOLMAP grant performed by Guest Research Fellows at AMOLF

Gore E. (2003). *A Study of the Interaction between Oil and Pigment through the Analysis of Cross-sections from Painting*, Postgraduate Diploma in the Conservation of Easel Paintings Final Year Project. Courtauld Institute of Art. London.

Frank Hoogland (2004). *Mass spectrometric identification of water extractable polymeric additives from artists' acrylic paint and acrylic paint samples from paintings*, University of Amsterdam, Master of Science thesis

Heleen Zuurendonk (2004). *Metal Carboxylates in oil paintings*, University of Leiden, Master of Science thesis.

Theodorakopoulos C. (2005). *The excimer laser ablation of picture varnishes. An evaluation with reference to light-induced deterioration.*, PhD dissertation Royal College of Art, London.

Buonaduce I. (2006). *Ilaria buonaduce (2006). A multi-analytical approach for the investigation of materials and techniques in the art of gilding.* PhD dissertation University of Pisa.

List of publications in the period 2002-2006

2002

- Van den Berg J.D.J., van den Berg K.J. and Boon J.J. (2002). Identification of non-cross-linked compounds in methanolic extracts of cured and aged linseed oil-based paint films using gas chromatography-mass spectrometry. *J. Chromatogr. A* 950, p.195-211.
- Boon J.J., Keune K. and Learner T.S. (2002). Identification of pigments and media from a paint cross-section by direct mass spectrometry and high-resolution imaging mass spectrometric and microspectroscopic techniques. In: 13th triennial meeting of ICOMCC in Rio de Janeiro (R. Vontobel ed.), James & James, London, (Preprints, 1) p. 223-230.
- Boon J.J. and Learner T.S. (2002). Analytical mass spectrometry of artists' acrylic emulsion paints by direct temperature resolved mass spectrometry and laser desorption ionisation mass spectrometry. *J. Anal. Appl. Pyrolysis* 64, p.327-344.
- Boon J.J., Van der Weerd J., Keune K., Noble P. and Wadum J. (2002). Mechanical and chemical changes in Old Master paintings : dissolution, metal soap formation and remineralization processes in lead pigmented ground/ intermediate paint layers of 17th century paintings. In: 13th triennial meeting of ICOMCC in Rio de Janeiro (R. Vontobel ed.), James & James, London, (Preprints, 1). p. 401-406.
- Keune K., Noble P. and Boon J.J. (2002). Chemical changes in lead-pigmented oil paints : on the early stage of formation of protrusions. In: Art 2002 : 7th international conference on non-destructive testing and microanalysis for diagnostics and conservation of the cultural and environmental heritage, (R. van Grieken, K. Janssens, L. Van'tdack and G. Meersman eds). University of Antwerp, Antwerp. CD-ROM [9 p.].
- Languri G.M. and Boon J.J. (2002). Mass spectrometry as a micro-analytical method to study Kassel earth (vandyke brown) pigments in oil paint. In: Art 2002: 7th international conference on non-destructive testing and microanalysis for diagnostics and conservation of the cultural and environmental heritage, edited (R. van Grieken, K. Janssens, L. Van'tdack and G. Meersman eds). University of Antwerp, Antwerp. CD-ROM, [5 p.].
- Languri G.M., Van der Horst J. and Boon J.J. (2002). Characterisation of a unique "asphalt" sample from the early 19th century Hafkenscheid painting materials collection by analytical pyrolysis MS and GC/MS. *J. Anal. Appl. Pyrolysis* 63, p. 171-196. plus the Erratum: p. 123-124, (vol 64).
- Noble P., Boon J.J., Wadum J. (2002). Dissolution aggregation and protrusion : lead soap formation in 17th century grounds and paint layers. *ArtMatters*, Waanders, Zwolle. 1, p. 46-61.
- Odlyha M., Van den Brink O.F., Boon J.J., Bacci M. and Cohen N.S. (2002) Damage assessment of museum environments using paint-based dosimetry. In: 13th triennial meeting of ICOMCC in Rio de Janeiro (R. Vontobel ed.), James & James, London, (Preprints 1). p. 73-79.
- Van der Weerd J., Brammer H., Boon J.J. and Heeren R.M.A. (2002). Fourier Transform Infrared microscopic imaging of an embedded paint cross-section. *Applied Spectroscopy* 56, p. 275-283.
- Van der Weerd J., Boon J.J., Geldof M., Heeren R.M.A. and Noble P. (2002). Chemical changes in old master paintings: dissolution, metal soap formation and remineralization processes in lead pigmented paint layers of 17th century paintings. *Zeitschrift für Kunsttechnologie und Konservierung* 16, p. 36-51.

2003

- Novotná P., Boon J.J., Van der Horst J. and Pacáková V. (2003). Photodegradation of indigo in dichloromethane solution. *Journal of Coloration Technology* 119, p. 121-127.

- Scalarone D., Van der Horst J., Boon J.J. and Chiantore O. (2003). Direct-temperature mass spectrometric detection of volatile terpenoids and natural terpenoid polymers in fresh and artificially aged resins. *Journal of Mass Spectrometry* 38, p. 607-617.
- Van den Berg K.J. and De Keijzer M. (2003). De rode lakken van Vincent van Gogh en de overgang van de natuurlijke naar de synthetische kleurstoffen. *kM*, 47, pp. 14-17.
- Van der Weerd J., Van Veen M.K., Heeren R.M.A. and Boon J.J. (2003). Identification of pigments in paint cross sections by reflection visible light imaging microspectroscopy. *Analytical Chemistry* 75, p.716-722.
- ## 2004
- Van den Berg J.D.J., Vermist N.D., Carlyle L., Hol apek M. and Boon J.J. (2004). The effects of traditional processing methods of linseed oil on the composition of its triacylglycerols. *Journal of Separation Science* 27, p.181-199.
- Boon J.J., Wyplosz N., Hoogland F., Duursma M., Keune K. and Learner T.S. (2004). Molecular characterization and mapping of twentieth-century synthetic organic pigments and additives in paints. In: *Modern art, New museums*, (A. Roy and P. Smith eds). International Institute for Conservation of Historic and Artistic Works, London. p. 219.
- Digney-Peer S., Burnstock A., Learner T.S., Khanjian H., Hoogland F. and Boon J.J. (2004). The migration of surfactants in acrylic emulsion paint films. In: *Modern art, New museums* (A. Roy and P. Smith eds), International Institute for Conservation of Historic and Artistic Works, London. p. 202-207.
- Katsibiri O. and Boon J.J. (2004). Investigation of the gilding technique in two post-byzantine wall paintings using micro-analytical techniques. *Spectrochimica Acta Part B* 59, p.1593-1599.
- Keune K. and Boon J.J. (2004). Enhancement of the static SIMS secondary ion yields of lipid moieties by ultrathin gold coating of aged oil paint surfaces. *Surface and Interface Analysis* 36, p.1620-1628
- Keune K. and Boon J.J. (2004). Imaging secondary ion mass spectrometry of a paint cross section taken from an early netherlandish painting by Rogier van der Weyden. *Analytical Chemistry* 76, p.1374-1385.
- Van Loon A. and Boon J.J. (2004). Characterization of the deterioration of bone black in the 17th century Oranjezaal paintings using electron-microscopic and micro-spectroscopic imaging techniques. *Spectrochimica Acta Part B* 59, p.1601-1609.
- Van Loon A., Boon J.J., Keune K. and Van der Horst J. (2004). Binding medium analysis of blue colored glazes on silver gildings on 17th and 18th century German polychrome sculpture. In: *Historische Polychromie: Skulpturenfassung in Deutschland und Japan* (M. Kühenthal and S. Miura eds), Hirmer Verlag, München. p. 352-379.
- Van der Weerd J., Geldof M., Struik van der Loeff L., Heeren R.M.A. and Boon J.J. (2004). Zinc soap aggregate formation in 'Falling Leaves; Les Alyscamps' by Vincent van Gogh. *Zeitschrift für Kunsttechnologie und Konservierung* 17, p.407-416.
- Van der Weerd J., Heeren R.M.A. and Boon J.J. (2004). Preparation methods and accessories for the infrared spectroscopic analysis of multi-layer paint films. *Studies in Conservation* 49, p.193-210.
- ## 2005
- Bommel, van M., Geldof M. and Hendriks E. (2005). Examination of the use of organic red pigments in paintings by Vincent van Gogh (November 1885 to February 1888), *ArtMatters* 3, pp 111-137.
- Boon, J.J., Gore E., Keune K. and Burnstock A. (2005). Image analytical studies of lead soap aggregates and their relationship to lead and tin in 15th C lead tin yellow paints from the Sherborne triptych. In: *IRUG6 Conference*. 2004. Florence, Italy; (M. Picollo ed). Il Prato, Padova, Italy. p.66-74.
- Boon, J.J., Ferreira E. S. B and Keune K. (2005). Imaging analytical studies of Old Master paints using FTIR, SIMS and SEMEDX of embedded paint cross sections, *Microscopy and microanalysis* (11), p 1370-1371
- Boon, J.J., Keune K. and Zucker J. (2005). Imaging analytical studies of lead soaps aggregating in preprimed canvas used by the Hudson River School painter F.E. Church, *Microscopy and microanalysis* (11), p 444-445
- Boitelle, R., Bosc M. and van den Berg K.J. (2005). Reflections on J.-F. Millet's *Agar et Ismaël*. Technical analyses of an unfinished painting. *ArtMatters* 2, p 7-21.

- Boitelle, R., Goetz E. and van den Berg K.J. (2005). A technical examination of Odilon Redon's paintings from the Bongor Collection, Van Gogh Museum, *ArtMatters* 3, pp 66-81.
- Burnstock A., van den Berg K.J. and Bubb R. (2005). A collection of artists' paint bladders from Gainsborough's house, *Zeitung für Kunsttechnologie und Konservierung*, 19, p. 264-272
- Burnstock A., Lanfear I., van den Berg K.J., Carlyle L., Clarke M., Hendriks E. and Kirby J. (2005). A comparison of the fading and surface deterioration of red lake pigments in six paintings by Vincent van Gogh with artificially aged paint reconstructions. In: *Proceedings of the 14th Triennial Meeting of ICOM Committee for Conservation in The Hague* (I. Vergier ed), James and James, London. Preprint vol. 1, p. 459-466.
- Burnstock A., van den Berg K.J. and Bubb R. (2005). Analysis of a rare collection of artists' paint bladders from Gainsborough's house c. 1800. In: *Proceedings of Art '05 the 8th International Conference on 'Non-Destructive Investigations and Micro analysis for the Diagnostics and Conservation of the Cultural and Environmental Heritage, Lecce (Italy)*, (C. Parisi, G. Buzzanca and A. Paradisi eds), ICR, Rome. paper on CD-ROM
- Burnstock A., van den Berg K.J. and House J. (2005). Painting techniques of Pierre-Auguste Renoir: 1868-1919. *ArtMatters* 3, p. 47-65.
- Carlyle L. and Witlox M. (2005). Historically Accurate Oil Painting Reconstructions. In: *Approaching the Art of the Past: Sources and reconstructions In: Art of the Past — Sources and Reconstructions* (M. Clarke, A. Stijnman, J.H. Townsend eds), Archetype Publications, London.. p. 53-60
- Clarke M. and Carlyle L. (2005). Page-Image Recipe Databases, a new approach for accessing art technological manuscripts and rare printed sources : The Winsor & Newton archive prototype. In: *Proceedings of 14th Triennial Meeting of the ICOM Committee for Conservation, The Hague* (I. Vergier ed), James and James, London, p. 24-29.
- Clarke M. and Carlyle L. (2005) "Page-Image Recipe Databases, a new approach to making art technological manuscripts and rare printed sources accessible." In: *Art of the Past — Sources and Reconstructions* (Clarke, M., Stijnman, A. Townsend, J.H. eds.) Archetype Publications, London, p. 49-52.
- Eastaugh N, Walsh V. and Boon J.J. (2005). The lazurite database: an image-based solution for recording and presenting data from painting studies. In: *Proceedings of the 14th Triennial Meeting of the ICOM Committee for Conservation in the Hague* (I.Vergier ed), James & James, London. Preprints volume 2, p 833
- Ferreira E.S.B., van der Horst J. and Boon J. J. (2005) Chemical aspects of the binding media of the Oranjezaal paintings, an insight into 17th century Netherlandish paintings. In: *Proceedings of the 14th Triennial Meeting of the ICOM Committee for Conservation in the Hague* (I.Vergier ed), James & James, London. Preprints volume 2, p.774-782
- Haswell R. and Carlyle L. (2006). Van Gogh's Painting Grounds: quantitative determination of bulking agents (extenders) using SEM/EDX, *Microchimica Acta*, 155, 162-169
- Hendriks E. and Geldof M. (2005). Van Gogh's Antwerp and Paris picture supports (1885-1888). Recreating choices. *ArtMatters* 2, pp 39-75
- Keune K., Ferreira E.S. B. and Boon J.J. (2005). Characterization and localization of the oil-binding medium in paint cross-sections using imaging secondary ion mass spectrometry. In: *Proceedings of the 14th Triennial Meeting of the ICOM Committee for Conservation in the Hague* (I.Vergier ed), James & James, London. Preprints volume 2, p. 796-802
- Keune K, and Boon J. J. (2005). Analytical Imaging Studies Clarifying the Process of the Darkening of Vermilion in Paintings. *Analytical Chemistry*, p. 4742-4750.
- Languri G.M., Boitelle R. and Boon J.J. (2005). Changing properties of the asphalt and oil in asphalt-oil paints prepared according to 19th century recipes. In: *Proceedings of the 14th Triennial Meeting of the ICOM Committee for Conservation in the Hague* (I.Vergier ed), James & James, London. Preprints volume 2, p.489-495
- Languri G.M. and Boon J.J. (2005). Between myth and reality: on the mummy pigment from the 19th-century Hafkenscheid collection. *Studies in Conservation* (50), pp. 161-178
- Leone B., Burnstock A., Jones C., Hallebeek P., Boon J.J. and Katrien Keune (2005). The Deterioration of

- Cadmium Sulphide Yellow Artists' Pigments, In: Proceedings of the 14th Triennial Meeting of the ICOM Committee for Conservation in the Hague (I.Vergier ed), James & James, London. Preprints volume 2, p 803-813
- Marino B., Boon J.J. and Hendriks E. (2005). Quantitative colour comparison of grounds and paints in paint cross-sections from a selection of paintings from the Paris period by Vincent van Gogh. In: Proceedings of the 14th Triennial Meeting of the ICOM Committee for Conservation in the Hague (I.Vergier ed), James & James, London. Preprints 2, pp. 814-823.
- Marino B., van de Horst J., Learner T.S. and Boon J.J. (2005). A mass spectrometric study of the naphthol PR170 as pigment and in paint acrylic emulsion paint. In: Dyes in History and Archaeology (J. Kirby ed), Archetype Publications, London. Volume 20, p. 187-197
- Marino B., Hendriks E. and Boon J.J. (2005). Quantitative imaging analytical studies of grounds and paints in a selection of paintings from the Paris period by Vincent van Gogh. In: Proceedings of the 14th Triennial Meeting of the ICOM Committee for Conservation in the Hague (I. Vergier ed), James & James, London. Preprints vol 2, p 814-823
- Marino B., Keune K., Hendriks E. and Boon J.J. (2005). SIMS Studies of the material aspects in grounds and paints in painting by van Gogh In: Proceedings of Art '05 the 8th International Conference on 'Non-Destructive Investigations and Micro analysis for the Diagnostics and Conservation of the Cultural and Environmental Heritage, Lecce (Italy) (C. Parisi, G. Buzzanca and A. Paradisi eds), ICR, Rome. paper on CD-ROM 12p.
- Noble P., Van Loon A. and Boon J.J. (2005). Chemical changes in old master paintings II: darkening due to increased transparency as a result of metal soap formation processes. In: Proceedings of the 14th Triennial Meeting of the ICOM Committee for Conservation in the Hague (I.Vergier ed), James & James, London. Preprints vol 2, p 496-503
- Odlyha M., Wade N., Wang Q., Campana R., Slater J.M., Svendsen M.R., Padfield T., De Santis F., Smith V.A., Bullock L., Ferreira E.S.B., Boon J.J., Pratt K. and Ormsby B. (2005) Microclimate indoor monitoring: damage assessment for cultural heritage preservation. In: Proceedings of the 14th Triennial Meeting of the ICOM Committee for Conservation in the Hague (I.Vergier ed), James & James, London. Preprints vol 2, p 670-676
- Richter M., Schäfer S. and Van Loon A. (2005). El tratado arte de la pintura de Francisco Pacheco y su influencia en la técnica de ejecución de las encarnaciones en la escultura alemana del siglo XVIII: primeros resultados obtenidos de análisis avanzados realizados en micromuestras. In: Investigación en conservación y restauración: Il congreso del grupo Español del IIC / ed. Museo nacional d'art de Catalunya. - Catalunya: Museo nacional d'art de Catalunya, p. 225-234.
- Scalarone D. Duursma M.C., Boon J.J. and Chiantore O. (2005). MALDI-TOF mass spectrometry on cellulosic surfaces of fresh and photo aged di-and triterpenoid varnish resins, Journal of Mass Spectrometry, 40, 1527-1535
- L. Speleers: A remarkable signature by Theodoor van Thulden in the Oranjezaal Art Matters 3, p.98-103
- Theodorakopoulos C., Zafiropulos V., Fotakis C., Boon J. J., van der Horst J., Dickmann K., and Knapp D. (2005). A study on the oxidative gradient of aged traditional triterpenoid resins using 'optimum' photoablation parameters, In: Proceedings of the Lacona-V September 15-18 2003, Osnabrück, Germany, (K. Dickmann, C. Fotakis and J.F. Asmus eds), Springer-Verlag, Berlin Heidelberg, p. 255-262
- Theodorakopoulos C., Zafiropulos V. and Boon J.J. (2005). Molecular study of the depth-dependent oxidation and condensation gradients of aged dammar and mastic varnish films assisted by KrF excimer laser ablation. In: Proceedings of the 14th Triennial Meeting of the ICOM Committee for Conservation in the Hague (I.Vergier ed), James & James, London. Preprints vol 2, p.836
- Van Eikema Hommes, M. H. (2005) The Contours in the Paintings of the Oranjezaal, Huis ten Bosch. In: The learned Eye, Regarding Art, Theory, and the Artists' Reputation (Weststeijn, T., et al. eds), Essays for Ernst van de Wetering, Amsterdam. p. 58-84.
- Van Eikema Hommes, M. H. (2005). Pieter de Grebber and the Oranjezaal in Huis ten Bosch, Part I: De Regulen (1649). Art Matters, 3. p. 20-36.
- Van Eikema Hommes M. and L. Speleers (2005). Pieter de Grebber and the Oranjezaal in Huis ten Bosch -part II:

variations in painting technique,
ArtMatters 3, 37-46.

Van Loon A. and Boon J.J. (2005).
Identifying and localizing proteinaceous
compounds in paint samples using
reflection FTIR. In: IRUG6 Conference
2004. Florence, Italy, (M. Picollo ed),
Il Prato, Padova, p.130-136

Van Loon A. Keune K. and Boon J. J.
(2005). Improving the surface quality of
paint cross-sections for imaging analy-
tical studies with specular reflection
FTIR and Static-SIMS. In: Conference
Proceedings Art 2005, 8th International
conference on non-destructive
investigations and microanalysis,
Lecce (Italy) (C. Parisi, G. Buzzanca and
A. Paradisi eds), ICR, Rome. Theme B
Microanalysis, contribution #089, p1-16,
paper on CD-ROM

Van Loon A. and J.J Boon (2005). The
Whitening of oil paints fims containing
bone black. In: Proceedings of the
14th Triennial Meeting of the ICOM
Committee for Conservation in the
Hague (I.Vergier ed), James & James,
London. Preprints vol 2, p. 511-518

Van der Weerd J., van Loon A., and
Boon J.J. (2005). FTIR studies of the
effect of pigments in the ageing of oil.
Studies in Conservation, 50 (1) p. 2-33

Witlox M. and Carlyle L. (2005).
A perfect ground is the very soul of the
art' (Kingston 1835): ground recipes for
oil painting, 1600-1900. In: Proceedings
of the 14th Triennial Meeting of the
ICOM Committee for Conservation in
the Hague (I.Vergier ed), James & James,
London. Preprints 1, p.519-530

2006

Boon J.J. and Asahina S., (2006) Surface
preparation of cross sections from
traditional and modern paint using the
Argon ion milling polishing CP system,
Microscopy and Microanalysis vol. 12,
p.1322-1323

Hendriks E. and Van Tilborgh L. (2006).
In Relation to Van Gogh; A Technical
and Art Historical Study of his Antwerp
and Paris Paintings in the Van Gogh
Museum , submitted as PhD thesis of
University of Amsterdam, Amsterdam,
The Netherlands

Osmond G., Keune K. and Boon,
J.J. (2006). A study of zinc soaps
aggregates in a late 19th century
painting by R.G. Rivers at the
Queensland Art Gallery, AICCM Bulletin,
vol. 29, 2005, p.37-46

Townsend J.H. and Keune K.(2006).
Microscopical techniques applied to
traditional paintings, Infocus Magazine,
p.54-65

Van Loon A., Speleers L., Ferreira E.,
Keune K., Boon J. J. (2006).
The relationship between the degree of
preservation and painting technique in
the Oranjezaal ensemble, Huis ten Bosch
palace. In: The Object in Context:
Crossing Conservation Boundaries
(D. Saunders et al eds), IIC, London,
p. 218-223

2007

Van Tilborgh L. and Hendriks E. (2007).
Vincent van Gogh Paintings II; Antwerp
and Paris 1885-1888, Van Gogh Museum
Amsterdam, Waanders, Zwolle, ca. 450
pages.

Submitted or in press

- Boon, J.J., Hoogland F.G. and van der Horst J. Mass spectrometry of modern paints, In: Proceedings of the Modern Paints Uncovered symposium held 16-19 mei 2006 in Londen. In press
- M. Clarke, P. Fredrickx, L. Speleers, I. Vanden Berghe, and J. Wouters. Comparative studies of seventeenth-century Netherlandish red lake glazes in the Oranjezaal, Palace Huis ten Bosch. DHA conference in Rigisberg. In press
- F. G. Hoogland, J. van der Horst and J.J. Boon. Liquefying oil paint in some late 20th century paintings. In: Proceedings of the Modern Paints Uncovered symposium held 16-19 mei 2006 in Londen. In press
- Hoogland F.G. and J.J. Boon. Poly(ethylene glycol) additives in acrylic emulsion media and paints analyzed by MALDI MS and nano ESI MS. Submitted to JMS.
- Ferreira E.S.B., Keune K. and J.J. Boon. Combined Microscopic Analytical Techniques as Diagnostic Tools in the Study of Paint Cross-sections: The case study of a sample from a 15th Century Painting 'The Descent from the cross' by Rogier van der Weyden, Proceedings of the 4th biennial meeting of the IPCR (Instituto Portugues de Conservacao e Restauro), Lisbon, 24-25 November 2005. In press
- Keune K. and Boon J.J. Insights into the lead soap aggregate formation in oil paintings with analytical imaging studies. Studies in Conservation, in press
- Speleers L. and van Eikema Hommes M. H. Jacob van Campen "Frederik Hendrik als krijgsman die het water beheerst" in: Book on the Oranjezaal/ ed. by Ekkart, R. - Zwolle: Waanders Publishers,
- Speleers L. and van Eikema Hommes M. H. C. van Everdingen "De geboorte van Frederik Hendrik" in: Book on the Oranjezaal/ ed. by Ekkart, R. - Zwolle: Waanders Publishers,
- Speleers L. and van Eikema Hommes M. H. S. de Bray "Deel van de triomfstoef met veroverde wapenen" in: Ekkart, R. [Ed]: Oranjezaal. - Zwolle: Waanders Publisher,
- Speleers L. and van Eikema Hommes M. H. Theodoor van Thulden "Deel van de triomfstoet met gevangenen" in: Book on the Oranjezaal/ ed. by Ekkart, R. - Zwolle: Waanders Publishers,
- Speleers L. and van Eikema Hommes M. H. Jacob Jordaens "Allegori op de tijd" in: Book on the Oranjezaal/ ed. by Ekkart, R. - Zwolle: Waanders Publishers,
- Speleers L. and van Eikema Hommes M. H. Theodoor van Thulden "Deel van de triomfstoet met olifant en schilderijen" in: Book on the Oranjezaal/ ed. by Ekkart, R. - Zwolle: Waanders Publishers,
- Speleers L. and van Eikema Hommes M. H. Pieter de Grebber: Deel van de triomf in: Book on the Oranjezaal/ ed. by Ekkart, R. - Zwolle: Waanders Publishers,
- Speleers L. and van Eikema Hommes M. H. Pieter Fransz. de Grebber "Deel van de triomf, met offerstier in: Book on the Oranjezaal/ ed. by Ekkart, R. - Zwolle: Waanders Publishers,
- Speleers L. and van Eikema Hommes M. H. Gerrit van Honthorst: De ontschepping van Maria Stuart in: Book on the Oranjezaal/ ed. by Ekkart, R. - Zwolle: Waanders Publishers,
- Speleers L. and van Eikema Hommes M. H. Gerrit van Honthorst: Allegorie op het huwelijk van Louise Henriette in: Book on the Oranjezaal/ ed. by Ekkart, R. - Zwolle: Waanders Publishers,
- Speleers L. and van Eikema Hommes M. H. Gerrit van Honthorst: Allegorie op het huwelijk van Frederik Hendrik in: Book on the Oranjezaal/ ed. by Ekkart, R. - Zwolle: Waanders Publishers,
- Speleers L. and van Eikema Hommes M. H. Gerrit van Honthorst: Deel van de triomf, Amalia en haar dochters in: Book on the Oranjezaal/ ed. by Ekkart, R. - Zwolle: Waanders Publishers,
- Speleers L. and van Eikema Hommes M. H. Jacob Jordaens: Frederik Hendrik als triomfator in: Book on the Oranjezaal/ ed. by Ekkart, R. - Zwolle: Waanders Publishers,
- Speleers L. and van Eikema Hommes M. H. Pieter Soutman "Deel van de triomfstoet met meegevoerd goud en zilver" in: Book on the Oranjezaal/ ed. by Ekkart, R. - Zwolle: Waanders Publishers,
- Speleers L. and van Eikema Hommes M. H. Solomon de Bray "Deel van de triomf, met muzikanten en veroverde vaandels" in: Book on the Oranjezaal/ ed. by Ekkart, R. - Zwolle: Waanders Publishers,
- Speleers L. and van Eikema Hommes M. H. Gerrit van Honthorst: Frederik Hendriks standvastigheid in: Book on

- the Oranjezaal/ ed. by Ekkart, R. - Zwolle: Waanders Publishers,
- Speleers L. and van Eikema Hommes M. H. Theodoor van Thulden "De Nederlandse maagd biedt Frederik Hendrik het opperbevel aan" in: Book on the Oranjezaal/ ed. by Ekkart, R. - Zwolle: Waanders Publishers,
- Speleers L. and van Eikema Hommes M. H. Thomas Willeboirts Bosschaert "Frederik Hendrik en Maurits als veldheren met in het verschiet de slag van Vlaanderen" in: Book on the Oranjezaal/ ed. by Ekkart, R. - Zwolle: Waanders Publishers,
- Speleers L. and van Eikema Hommes M. H. Theodoor van Thulden "De opvoeding van Frederik Hendrik" in: Book on the Oranjezaal/ ed. by Ekkart, R. - Zwolle: Waanders Publishers,
- Speleers L. and van Eikema Hommes M. H. Theodoor van Thulden "Venus in de winkel van Vulcanus" in: Book on the Oranjezaal/ ed. by Ekkart, R. - Zwolle: Waanders Publishers,
- Speleers L. and van Eikema Hommes M. H. Theodoor van Thulden "De smidse van Vulcanus" in: Book on the Oranjezaal/ ed. by Ekkart, R. - Zwolle: Waanders Publishers,
- Speleers L. and van Eikema Hommes M. H. Caesar van Everdingen "vier Muzen en Pegasus" in: Book on the Oranjezaal/ ed. by Ekkart, R. - Zwolle: Waanders Publishers,
- Speleers L. and van Eikema Hommes M. H. Jan Lievens "Vijf Muzen" in: Book on the Oranjezaal/ ed. by Ekkart, R. - Zwolle: Waanders Publishers,
- Speleers L. and van Eikema Hommes M. H. Jacob van Campen "Apollo op de zonnwagen." in: Book on the Oranjezaal/ ed. by Ekkart, R. - Zwolle: Waanders Publishers,
- Speleers L. and van Eikema Hommes M. H. Gonzales Coques, de survivantie in: Book on the Oranjezaal/ ed. by Ekkart, R. - Zwolle: Waanders Publishers,
- Speleers L. and van Eikema Hommes M. H. Jacob van Campen "Deel van de triomfstoet met geschenken uit de Oost en West" in: Book on the Oranjezaal/ ed. by Ekkart, R. - Zwolle: Waanders Publishers,
- Speleers L. and van Eikema Hommes M. H. Thomas Willeboirts Bosschaert "Frederik Hendrik als heerser over de zeeën" in: Book on the Oranjezaal/ ed. by Ekkart, R. - Zwolle: Waanders Publishers,
- Speleers L. and van Eikema Hommes M. H. P. Soutman "Allegorie op het goede bestuur" in: Book on the Oranjezaal/ ed. by Ekkart, R. - Zwolle: Waanders Publishers,
- Eikema Hommes, M. H. van, A remarkable seventeenth-century light concept: The rendering of light in the paintings in the Oranjezaal, Huis ten Bosch. In preparation for the Book on the Oranjezaal/ ed. by Ekkart, R. - Zwolle: Waanders Publishers,
- Van Eikema Hommes, M. H. and Speleers L. (2006). Comparative Studies of Pictorial and Technical Means in the Oranjezaal: Nine Muses', submitted to Zeitschrift für Kunsttechnologie und Konservierung.

List of presentations in the period 2002-2006

2002

COST Action G8 ,Non-destructive Analysis and Testing of Museum Objects, Ghent, Belgium 25 January 2002. K. Keune and J.J. Boon
Imaging mass spectrometry and microspectroscopy of paintings cross-sections.

International Symposium on Analytical Pyrolysis of Polymers, Nagoya, Japan, 24-25 January 2002. J.J. Boon and T. Learner. Analytical mass spectrometry of artist's acrylic emulsion paints by direct temperature resolved mass spectrometry and laser desorption ionisation mass spectrometry.

Presentation for the Courtauld Institute students, AMOLF, Amsterdam, 12 March 2002
J.J. Boon. Methods of analysis and new ideas on the composition of oil paint.

SIMS Conference, University of Siena, Department of Chemical and Biosystem Sciences and Technologies, Siena, Italy, 21-22 March 2002
K. Keune, R. Heeren and J.J. Boon.
Imaging mass spectrometry and microspectroscopy of paintings cross-sections.

Center for Art Diagnosis and

Hagiography, Ormylia, Greece, 16 May 2002

J.J. Boon. MOLART painting studies at AMOLF

De Mayerne opening symposium, Rijksmuseum Amsterdam, 28 May 2002.

J.J. Boon. The De Mayerne MOLMAP project: Imaging microspectroscopy and mass spectrometric microscopy of paint cross-sections as tools to study aging processes in oil paintings

L. Speleers and M. van Eikema-Hommes. Pictorial illusion and technique: comparative studies of three paintings in the Oranjezaal

M.H. van Eikema Hommes and Lidwien Speleers. The influence of the positioning of the paintings in the Oranjezaal on painting technique.

L. Carlyle. Historically Accurate Reconstructions of Artists' Materials: The HART project.

Symposium on Smalt, Centraal Museum, Utrecht, 30 May 2002.

J.J. Boon and K. Keune. Chemical changes in smalt and lead white containing layers in Old Master paintings.

PV lecture for Colloid Chemistry, Universiteit Utrecht, Uithof, 31 May 2002.

J.J. Boon. Schilderij onderzoek als uitdaging voor chemici.

ART 2002, Antwerp, 2-6 June 2002.

K. Keune, P. Noble and J.J. Boon.

Chemical changes in lead-pigmented oil paints: on the early stage of formation of protrusions.

G. Languri and J.J. Boon. Mass spectrometry as a microanalytical method to study Kassel Earth (Vandyke brown) pigments in oil paint. (poster).

Lunch time lecture at NWO, Den Haag, 4 July 2002.

L. Carlyle. Introduction into the De Mayerne Programme and the HART project.

Programme committee De Mayerne, AMOLF, Amsterdam, 11 September 2002.

K. Keune. An analytical approach in the studies of paint cross-sections
J.J. Boon Zinc soaps in aged lead chromate paints in Van Gogh paintings

Secondary Ion Mass Spectrometry Europe 2002, Münster, 15-17 September, 2002

K. Keune, P. Noble and J.J. Boon. Secondary Ion Mass Spectrometry on Paint-Cross-Sections. (poster)

KNCV Najaarscongres 2002: Chemie en Schilderkunst, Den Haag, 19 September 2002.

J.J. Boon. Schilderijen onderzoek:

- een uitdaging voor chemici.
L. Carlyle. Historically accurate reconstructions: a tool in the history of painting.
- 13th Triennial Meeting of ICOMCC, Rio de Janeiro, 23-28 September 2002.
J.J. Boon, K. Keune and T. Learner. Identification of pigments and media from a paint crosssection by direct mass spectrometry and high-resolution imaging mass spectrometric and microspectroscopic techniques
M. Odlyha, O.F. van den Brink, J.J. Boon, M. Bacci, N.S. Cohen. Damage assessment of museum environments using paint based dosimetry
J.J. Boon, J. van der Weerd, K. Keune, P. Noble, and J. Wadum. Mechanical and chemical changes in Old Master paintings: dissolution, metal soap formation and remineralization processes in lead pigmented ground/intermediate paint layers of 17th century paintings.
- Netherlands Society of Mass Spectrometry NVMS, University of Twente, Enschede, 4 oktober 2002.
K. Keune, P. Noble and J.J. Boon. Secondary Ion Mass Spectrometry on Paint-Cross-Sections. (poster)
- 21st Annual Meeting on Dyes in History and Archaeology, Avignon et Lauris, France, 10-12 October 2002.
M. Clarke. "Half of Nothing"-New developments in non-sampling spectroscopy for very small specimens of organic pigments. (poster).
- Instituut Collectie Nederland (ICN), Amsterdam, 24 October 2002.
L. Carlyle. On the development of oil
- paint colors in the 19th century.
M. Clarke. Pigments: history, analysis, contemporary recipe books, reconstructions
- Allied Circle, Den Burg, Texel, 7 November 2002.
J.J. Boon. Schilderij onderzoek Instituut Collectie Nederland (ICN), Amsterdam, 18 November 2002.
L. Carlyle. Historical reconstructions of paintings.
- Art Institute of Chicago, Chicago, USA. 26 November 2002.
J.J. Boon. Phenomenology, chemistry and dynamics of metal soap aggregates and protrusions in 17th and 19th century paintings .
- Stichting Restauratie Ateliers Limburg, Maastricht, 2-4 December 2002.
L. Carlyle. Three-day course in oil painting materials and techniques from the 17th and 19th century.
- 2003**
- AMOLF, Amsterdam, 31 January 2003.
K. Keune. Imaging mass spectrometry and microspectroscopy of paint cross-sections.
- Separation and characterization of natural and synthetic macromolecules, Amsterdam, 5-7 February 2003.
J.J. Boon. Mass spectrometric characterisation and visualization of aged natural synthetic polymers in old master paintings
- Colloquium Chemie Universiteit Leiden, Leiden, 5 March 2003.
J.J. Boon. Old master paintings and
- danger: metal soaps pose alarming problems.
- Sackler Colloquium on Scientific Examination of Art, Washington, 20-21 March 2003.
J.J. Boon. Dynamic interactions in ageing paintings.
- Labstech Workshop on binding medium identification in art objects, ICN, Amsterdam, 27 March 2003.
J.J. Boon. Direct mass spectrometry of paint materials and samples from paintings and polychrome sculpture.
K. Keune. The imaging SIMS technique as tool to study pigment, binding media and metal soap distribution in paint cross sections from oil paintings
- Colloquium Chemie, Universiteit Groningen, 17 April 2003.
J.J. Boon. Complex chemical processes in old masters paintings.
- Stichting Lucas van Leijden, Stedelijk Museum de Lakenhal, Leiden, 23 May 2003.
J.J. Boon. Geavanceerd onderzoek van schilderijen: een kijkje onder het oppervlak
- NEVAC symposium, Leiden, 23 May 2003.
J.J. Boon. Old master paints develop into multilayer ionic polymer composites
- MOLART Highlights day, Van Gogh Museum, Amsterdam, June 19, 2003.
J.P. Filedt-Kok. Welcome and opening remarks
J.J. Boon. The MOLART programme 1995-2002: a research programme on molecular aspects of ageing in paintings

- A. Wallert. 17th C paintings: original intent, present appearance
M.H. van Eikema-Hommes. Indigo as a pigment in oil painting and the problem of fading.
K.J. van den Berg. Material's use and colour changes in paintings
L.B.J. Speleers and M.M. te Marvelde. Research on the restoration history and material properties of paintings in the Oranjezaal.
J.D.J. van der Berg and K. Keune. Characterisation and localisation of the constituents of traditional oil paints .
P. Noble, K.Keune and J.J. Boon. Further insights into protrusion formation: metal soap formation in lead and zinc-containing paint layers.
J.R.J. van Asperen de Boer. Infrared reflectography: in the MOLART project
A. Burnstock. The relevance of MOLART for conservation
ICXOM XVII, Chamonix, 22-26 September 2003
A. van Loon, L. Speleers and J.J. Boon. The study of the deterioration of bone black in the 17th C Oranjezaal paintings using advanced analytical imaging techniques
K. Keune and J.J. Boon. Identification and surface modification of aged oil paint revealed with SIMS
O. Katsibiri and J.J. Boon. Investigation of two Post Byzantine wall paintings using micro-analytical techniques.
Reinwardt Academy, Amsterdam, 6 October 2003
K. Keune. Analytical methods for investigation of painting
Kleijn Colloquium, AMOLF, Amsterdam, 6 October 2003
K. Keune and J.J. Boon. Identification and surface modification of aged oil paint revealed with SIMS
SRAL, Maastricht, 27 October 2003
J.J. Boon. A critical evaluation of cleaning of paintings in the light of MOLART's model of aged oil paint
DHA 22 conference, Riggisberg, 24-27 October 2003.
M. Clarke, P. Fredrickx, L. Speleers, I. Vanden Berghe, and J. Wouters. Comparative studies of seventeenth-century Netherlandish red lake glazes in the Oranjezaal, Palace Huis ten Bosch.
Quality control for restoration materials and techniques, Rijksmuseum Twente, 22 November 2003.
J.J. Boon. Concerns about cleaning
VU, Amsterdam, 26 November 2003
J.J. Boon.. Moleculair schilderijonderzoek van Oude Meesters
Presentation for Master Students of the Reinwardt Academy, AMOLF, 10 December 2003. K. Keune. Analytical methods for investigation of paintings
2004
Department of Material Science, TUD, Delft, 20 Januari 2004
J.J. Boon. Old Master paintings are dynamic systems
Stichting PAC Symposium, VU, Amsterdam, 4 March 2004
J.J. Boon. Dynamische processen in schilderijen zijn een uitdaging voor de chemicus
IRUG 6 Conference, Florence, 29 March - 1 April 2004
J.J. Boon, E. Gore, K. Keune and A. Burnstock. Image analytical studies of lead soap aggregates and their relationship to lead and tin in 15th C lead tin yellow paints from the Sherborne triptych.
A. van Loon and J.J. Boon. Identifying and Localizing Proteinaceous Compounds in Paint Samples using Reflection Infrared Spectroscopic Techniques.
MaSC (Mass Spectrometry and Chromatography user's group), National Gallery of Art, Washington, USA, 7-8 april 2004
E.S.B. Ferreira, J. van der Horst, J.J. Boon. Curie point Py-GCMS at AMOLF, old knowledge, new setup.
Van den Berg K.J., Tsouli M. and Carlyle L. On the significance and reproducibility of molecular markers in GC analysis of aged oil paint.
American Institute for Conservation 2004 meeting in Portland, USA, 9-14 June 2004
J.J. Boon, F. Hoogland, E. Ferreira, G. van der Doelen, P. Novotna and G. Languri. Molecular Aspects of the Photochemistry of Varnish, Dyes and Drying Oils Studied in Photosensitising Solutions.(lecture)
J.J. Boon. Dosimeters made with tempera paint.
Euroanalysis XIII, Salamanca, Spain, 5-10 September 2004.
J.J. Boon, A van Loon and K. Keune. Imaging analytical studies of paint cross sections from Old Masters paintings

- MIMIC (Microclimate Indoor Monitoring In Cultural Heritage Preservation) project final meeting, Padua, Italy, 9 November 2004.
E.S.B. Ferreira, J. van der Horst, and J.J. Boon. DTMS analysis of Egg Tempera Dosimeters
- 20th international IIC congress on “Modern Art, New Museums”, Bilbao, Spain, 13-18 September 2004
J.J. Boon, N. Wyplosz, F. Hoogland, M. Duursma, K. Keune and T. Learner. Molecular characterization and mapping of 20th century synthetic organic pigments and additives in paints. (poster). S. Digney-Peer, A. Burnstock, T. Learner, H. Khanjian, F. Hoogland and J.J. Boon.
The Migration of Surfactants in Acrylic Emulsion Paint Films on Curing, Ageing and after Selected Surface Treatment.
- First Study group Art Technological Source Research (ATSR) meeting, Approaching the Art of the Past. Sources & Reconstructions, Instituut Collectie Nederland (ICN), Amsterdam, 14 October and 15 October 2004
Clarke M. and Carlyle L. (2005). Page-Image Recipe Databases, a new approach to making art technological manuscripts and rare printed sources accessible.
Carlyle L. and Witlox M. (2005). Historically Accurate Oil Painting Reconstructions.
- Fysica en Samenleving Lecture Series, Department of Physics, University of Leiden, Leiden, 15 October 2004.
J.J. Boon. Dynamic processes in Old Master paintings
- NWO De Mayerne Symposium, WCTW, Amsterdam, 19 November 2004
S. Bennet and E. Hendriks. Van Gogh in Paris.
J.J. Boon. MOLMAP-Imaging analytical studies of paint cross sections.
J.J. Boon and M. Faries. Proposed technical studies on preparatory layers.
L. Carlyle. Progress report: Historically accurate reconstructions.
K. Keune and J.J. Boon. How red old master paint transforms into black and white.
M. Clarke. Page Image Recipe Databases, a new approach for accessing art technological manuscripts and rare printed sources: The Winsor & Newton archive prototype.
M. Faries. Research plan of the project underdrawings.
A. van Grevenstein. Comparative Studies of Paintings in the Oranjezaal.
B. Marino, J.J. Boon and E. Hendriks. Image analytical studies of grounds used by Van Gogh.
L. Speleers and M. van Eikema Hommes. Comparative studies of paintings in the Oranjezaal The Oranjezaalproject: evaluation and results.
Y. Shimadzu. Transparency in 19th paintings.
M. Verhoeven. Deterioration processes in old master piece painting: Solid-state MAS NMR on paint models and historically accurate reconstructions.
M. Witlox. Historical Recipe Database-Ground recipes for oil painting: 1600-1900.
- 2005**
- Molecula Delicti*, Sigma symposium, Katholieke Universiteit Nijmegen, 17 Maart 2005
J.J. Boon. Laagopbouw en chemie van verflagen in Oude Meesters als criterium voor authenticiteit. Invited
- Separating Layers – Layer Separation Examination and Consolidation of European Sculpture Polychromy Symposium. Munich (Germany). 4-6 March 2005.
A. van Loon and J.J. Boon. “Separating” Layers in Paint Cross-Sections using Advanced Analytical Imaging.
Stephan Schaefer. Fluorescent probes in art and materials research or “100 years of staining”
- Washington and Lee University Student presentation, AMOLF, 14 April 2005
J.J. Boon. Dynamic processes in paintings.
- Art’05 Conference on Non-destructive Testing and Microanalysis for the Diagnostics and Conservation of the Cultural and Environmental Heritage. Lecce (Italy). 15-19 May 2005.
A. van Loon, K. Keune, and J.J. Boon. Improving the surface quality of paint cross-sections for imaging analytical studies with specular reflection FTIR and static-SIMS.
B. Marino, K. Keune, E. Hendriks and J.J. Boon (poster). ‘Material Aspects in Grounds and Paints in Paintings by Van Gogh Studied by SIMS.
A. Burnstock, K.J. van den Berg and R. Bubbs, Analysis of a rare collection

- of artists' paint bladders from Gainsborough's house c. 1800.
- Schlumberger Brainstorm Meeting on "Art et Chimie", Les Treilles Estate (près Tourtour near Draguignan), France, 20-25 May 2005
J.J. Boon. Art and Chemistry -*Personal Adornment*- ~ Chemistry of Art -*Molecular Studies of Paintings*-.
On invitation by Prof. Guy Ourisson.
K.Keune. Binding medium, pigments and metal soaps characterized and localized in paint cross sections.
On invitation by Prof. Guy Ourisson.
- Kleijn colloquium, AMOLF, Amsterdam, The Netherlands, 13 June 2005
K.Keune. Binding medium, pigments and metal soaps characterised and analysed in paint cross-sections,
- KNCV Atoomspectroscopie Werkgroep Lezingendag, Nederlands Forensisch Instituut, Rijswijk, The Netherlands, 10 June 2005
J.J. Boon, K.Keune and A. van Loon. Imaging Analytical Studies of Old Master Paints.
On invitation by the chairman.
- Studiemiddag Amsterdams Centrum voor de studie van de Gouden Eeuw: Nieuw licht op de Oranjezaal in Huis ten Bosch, Amsterdam, 24 June 2005.
M.H. van Eikema Hommes and L. Speleers. Het bijzondere lichtconcept in de Oranjezaal
- Microscopy and Microanalysis 2005 (M&M2005), Honolulu, USA, 1-5 August 2005
J.J. Boon, K. Keune, and J. Zucker. Imaging analytical studies of lead soaps aggregating in preprimed canvas used by the Hudson River School painter F. E. Church (1826-1900).
J.J. Boon, E. S. B. Ferreira and K. Keune.
Imaging analytical studies of Old Master paints using FTIR, SIMS and SEMEDX of embedded paint cross sections. (poster).
MaSc Conference, organised by the Users' group for Mass Spectrometry and Chromatography in Conservation (MaSc), Van Gogh Museum, Amsterdam, The Netherlands, 9 and 10 September 2005.
F.G. Hoogland, M.C. Duursma, T.J.S. Learner and J.J. Boon.
Full characterization of poly(ethylene glycol) based additives in acrylic paints by matrix-assisted laser desorption/ionisation mass spectrometry and nano-electrospray ionisation mass spectrometry.
Summerschool MaSc (Users' group for Mass Spectrometry and Chromatography in Conservation), AMOLF Amsterdam, The Netherlands, 7 and 8 September 2005
J.J. Boon. Tutorial lecture: Analytical mass spectrometry of acrylic emulsion paints by DTMS and LDMS
J.J. Boon. Tutorial lecture: Tempera paints used as dosimeters
J.J. Boon. Tutorial lecture: Molecular Aspects of the Photochemistry of Varnish and
J.J. Boon. Tutorial training: DTMS analysis of submitted samples.
Drying Oils Studied in Photosensitising Solutions
K. Keune. Tutorial lecture: Application of SIMS in the conservation field.
K. Keune and E. Ferreira. Tutorial training: SIMS studies of submitted samples.
- Metal Soaps Symposium organised by the Scientific Research Working Group of ICOM-CC, Van Gogh Museum, Amsterdam, 10 September 2005.
F.G. Hoogland and J.J. Boon.
Monitoring the reaction of fatty acid moieties in paint films.
K.Keune and J.J. Boon. Image analytical studies of metal soaps in paint cross sections in oil painting from 15th-20th Century unveil aspects of their mode of formation.
ICOMCC-2005, 14th Triennial Meeting of the ICOM Committee for Conservation. The Hague, 12-16 September 2005.
M. Clarke and L. Carlyle (2005).
Page-Image Recipe Databases, a new approach for accessing art technological manuscripts and rare printed sources
N. Eastaugh, V.Walsh and J.J. Boon. The Lazurite database: an image based solution for recording and presenting data from painting studies (poster).
E.S.B. Ferreira, J. van der Horst, and J.J. Boon. Chemical aspects of the binding media of the Oranjezaal paintings, an insight into 17th century Netherlandish paintings.
I. Lanfear, A. Burnstock, K.J. van den Berg, L. Carlyle, M. Clarke, E. Hendriks and J. Kirby. J. A comparison of the fading and surface deterioration of red lake pigments in six paintings by Vincent van Gogh with artificially aged paint reconstructions.
B. Marino, E. Hendriks and J.J. Boon. Quantitative imaging analytical studies of grounds and paints in a selection of paintings from the Paris period by Vincent van Gogh.
P. Noble, A. Van Loon and J.J. Boon. Chemical changes in old master

- paintings II: darkening due to increased transparency as a result of metal soap formation processes. G.M. Languri, R. Boitelle and J.J. Boon. Changing properties of the asphalt and oil in asphalt-oil paints prepared according to 19th century recipes.
- B. Leone, A. Burnstock, C. Jones, P.Hallebeek, J.J. Boon, and K. Keune. The Deterioration of Cadmium Sulphide Yellow Artists' Pigments. K. Keune, E.S.B. Ferreira and J.J. Boon. Determination of the distribution and speciation of monocarboxylic fatty acids in embedded paint cross sections using secondary ion mass spectrometry. M. Odlyha, N. Wade, J.M. Slater, Q.Wang, R. Campana, B. Ormsby, M. Rhyl Svendsen, T. Padfield, F. De Santis, V. Smith, L. Bullock, E.S.B. Ferreira, and J.J. Boon. Microclimate Indoor Monitoring Damage assessment for Cultural Heritage Preservation.
- C. Theodorakopoulos, V.Zafiriopoulos and J.J. Boon. Molecular study of the depth-dependent oxidation and condensation gradients of aged dammar and mastic varnish films assisted by KrFexcimer laser ablation (poster). K.J. Van den Berg, C. Maines, E.S.B. Ferreira, C. Higgitt, and K. Sutherland. The Users' Group for Mass Spectrometry and Chromatography and the development of a mass spectral database for the study of artistic and cultural objects. K.J. Van den Berg, A. Burnstock, L. Carlyle, M. Clarke, E. Hendriks, J. Kirby, I. Lanfear and R. Hoppenbrouwers. Relative rates of fading of red lake paints after Vincent van Gogh.
- A. Van Loon and J.J. Boon. The whitening of oil paint films containing bone black. M. Witlox and L. Carlyle (2005). 'A perfect ground is the very soul of the art' (Kingston 1835): ground recipes for oil painting, 1600-1900. Dutch Society for Microscopy, KREM Annual meeting, CBS Utrecht, The Netherlands, 28 September 2005
- J.J. Boon. Ion beam cross sectioning and polishing: First experiences. P.J. Block Jaarlijkse Lezing, Kamerlingh Onnes Gebouw, Leiden, The Netherlands, 24 October 2005
- J.J. Boon. Schilderijen veranderen voortdurend en baart dat zorgen? On invitation by de Vereniging Oud Leiden, De Leidse Universiteit and De Leidse Courant
- 2nd Congress of the Spanish IIC Group, Barcelona, 9-11 November 2005
- M.Richter, S.Schaefer and A van Loon. El tratado *Arte de la Pintura* de Francisco Pacheco y su influencia en la technical de ejecucion de las encarnaciones en la escultura alemana del siglo XVIII: primeras resultados obtenidos de analisis avanzados realizados en micro-muestras. The TATE, London, UK, 14 November 2005
- J.J. Boon. Chemical microscopy of paint cross sections: Imaging metal soaps and related oil paint defects. On invitation by the Head of Conservation. Restauratoren Tagung 2005, Deutscher Restauratoren Verband, Berlin, 18 november 2005.
- M.H. van Eikema Hommes. The painted decoration in the Oranjezaal, Huis ten Bosch: the interrelation between visual concept and painting methods
- Meeting of the IPCR (Instituto Português de Conservação e Restauro), Lisbon, Portugal, 24-25 November 2005.
- E.S.B. Ferreira, K. Keune, J.J. Boon, "Combined Microscopic Analytical Techniques as Diagnostic Tools in the Study of Paint Cross-Sections: Case study of a sample from a 15th century painting, *The Descent from the Cross* by Rogier van der Weyden".
- 2006**
- Modern paints uncovered (MPU), Tate Modern, London (UK), 16-19 May 2006.
- J.J. Boon Mass spectrometry applied modern paints (oral)
- F.G. Hoogland and J.J. Boon, Liquefying oil paint in some late 20th century paintings (poster)
- IRUG 7, MOMA, New York, 28-31 March 2006
- A. van Loon and J.J. Boon. The whitening of oil paint films containing bone black: a combined study of specular FTIR and SEM-EDX
- American Institute for Conservation Meeting 2006, Providence Rhode Island (USA), 16-19 June 2006.
- Paintings Working group: J.J. Boon. F.G. Hoogland, K.Keune. Chemical processes in aged oil paints leading to metal soap migration and aggregation
- J. Zucker and J.J. Boon. Opaque to

transparent: insights on bloom, haziness, protrusions and variable translucency from the Hudson River school and the Church archive. K. Keune, K. Kirsch and J.J. Boon. (poster). Lead soap efflorescence in a 19th C painting: appearance, nature and sources of materials. J.J. Boon, J. van der Horst, F.G. Hoogland, B. Marino and S. Asahina (poster). Argon ion milled cross section polishing of paint cross sections as an alternative for mechanical polishing and microtoming. Research and Technical Studies Group: B. Marino, E. Hendriks, François Horréard, François Hillion, and J.J. Boon. Imaging SIMS and NanoSims studies of Barite-Celestite particles in grounds of Van Gogh paintings

Microscopy and Microanalysis 2006, Chicago, 30 July-4 August 2006 J.J. Boon, J. van der Horst and S. Asahina (poster). Surface preparation of cross sections from traditional and modern paint using the Argon ion milling polishing CP system

Metropolitan Museum, Scientific Department, 23 May 2006 J.J. Boon: Metal soap in paintings: history, appearance and potential threat.

COST G8 ACTION: Non-destructive analysis and testing of museum objects. Final Meeting, Nicosia, Cyprus, 18-21 May 2006. J.J. Boon, Imaging chemical microscopy of metal soap reactivity in oil paintings

IIC meeting on The Object in Context: Crossing Conservation Boundaries, Munich, 28-1 September 2006 Annelies van Loon, Jaap J. Boon, Ester Ferreira, Katrien Keune, Lidwien Speleers. The relationship between the degree of preservation and painting technique in the Oranjezaal ensemble, Huis ten Bosch Palace (The Hague).

The National Portrait Gallery, Edinburgh, Scotland, 19 October 2006. Hendriks E., Van Gogh's painting materials and techniques; Paris encounters.

