Divisions for Physical Sciences, Chemical Sciences and Humanities
Research programme on molecular studies in conservation and technical studies in art history

De Mayerne Symposium
19 November 2004

The Netherlands Organisation for Scientific Research

De Mayerne
PROGRAMME

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The Hague, 19 November 2004
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Preface

De Mayerne research programme midway

About the impact of the De Mayerne programme I like to cite a recent letter of the Van Gogh museum to the director of the Amolf-institute: ‘In fact it is no exaggeration that the cumulative results emerging from the MOLART and DE MAYERNE programmes have transformed our way of looking at old master paintings. Contrary to established thought, aged oil paint films have now been shown to remain highly mobile systems in which degradation processes still continue to take place.’

In 2001 and 2003 eight research proposals were awarded within the framework of the multidisciplinary programme De Mayerne. All these projects are characterized by a variety of disciplines working together - analytical chemists, physicists, restorers as well as art historians. Aside from a strong interaction between the disciplines involved, there is also a strong coherence between the different projects of the programme.

The speakers of this symposium are all working on these projects. Today they will unravel the research outcomes so far and present concrete research plans for the near future. This midway symposium held for a broad audience of conservators, scientists and art historians gives maximum opportunity for comments and feedback.

Today’s speakers will shed light on a wide variety of research issues. How to reconstruct historically accurate oil paint and how to create an accurate recipe database for oil paintings? These are some of the questions addressed in the morning session by Carlyle, Witlox and Clarke. Faries and Van Loon will go into their research plan on the evaluative studies of infrared reflectography of paintings. Subsequently Marino will discuss the quantitative analysis of cross sections from selected grounds used by van Gogh. While after the lunch break, Boon will widen our knowledge about the materials and the application methods used by different artists and Keune throws new light on the photo induced chemical changes of vermilion paint on 17th century paintings.

The formation of protrusions on oil paintings was the reason for the research project *coordination chemistry of lead carboxylates and carbonates,* which was finalized last September. The outcomes of this project will be presented by Verhoeven. The influence of painting methods and materials on the present appearance of 19th century paintings will be elaborated on by Shimadzu. Finally, after the tea break, Grevenstein, Speleers and Eikema Hommes will focus on the research done during the restoration of the 44 allegorical 17th century Dutch and Flemish paintings in the Oranjezaal.

Abstracts of most of the above mentioned presentations can be found in this brochure.

I am convinced this symposium will once more demonstrate the vital relevance of fundamental scientific research to issues of cultural preservation. Hopefully the final findings of this programme will further widen our knowledge about the old master paintings.

Jan Piet Filedt Kok
Chairman of the Programme Committee;
Keeper of Paintings Rijksmuseum-Amsterdam

Who was De Mayerne?

Sir Theodore Turquet de Mayerne (23 Nov. 1573- 22 March 1655) 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). De Mayerne presented the many recipes and instructions in the manuscript in a straightforward manner and experimented practically, adding his comments and results in the margin of the text. These recipes and notes are derived from miscellaneous sources like old treatises on painting techniques. However, his main source of information was formed by the many conversations he had with diverse artists, including Rubens, Daniel Mijtens and Athony van Dyck.
De Mayerne can be seen as the first conservation scientist and his manuscript is still used as one of the main sources on 17th century painting techniques.

De Mayerne research programme

The De Mayerne research programme aims to foster and strengthen collaboration between art sciences and physical sciences by funding cross-disciplinary projects that focus on molecular studies in conservation and technical studies in art history. The budget for the programme is made available by the joint NWO Divisions for Humanities (GW), for Chemical Sciences (CW) and for Physical Sciences (EW).

The areas of research chosen for the De Mayerne programme are:

A Technical studies of paintings;
B Changes in material properties of paints, glazes and varnishes;
C Effects of restoration procedures;
D Method development, new instrumentation and data management.

Within the set-up of the programme cross-disciplinary project clusters, that group together several research topics, have been formed. Research groups from different institutions tightly collaborate within a project cluster.

The mission of the De Mayerne programme is to establish a strong cross-disciplinary central research programme on technical studies in art history and molecular conservation studies of art objects in the Netherlands. It intends to stimulate the participation of the natural sciences in the analysis and solution of art technical and conservation problems in paintings and related art objects.
The research programme intends to give a better insight in studio practices of painters, in ageing processes in works of art and the effects of conservation practices, which is of great importance for the preservation of our cultural heritage. Special attention is given to the multidisciplinarity of the projects and their application in art history, art chemistry and in conservation practice.

Below an overview is given of the awarded research proposals within the framework of the De Mayerne Programme.

First round 2001-2006

- “Comparative studies of paintings in the Oranjezaal” (SRAL, AMOLF, RUG).
- “Coordination chemistry of lead carboxylates in oil paintings” (SRAL, UL, AMOLF, Rijksmuseum, ICN, Mauritshuis).
- “Imaging and structural analysis of media and pigments in cross sections of paintings” (AMOLF, Rijksmuseum, Mauritshuis, Van Gogh Museum, SRAL, ICN, Tate Gallery).
- “Historically accurate reconstructions of oil paint and painting composites” (ICN, TU/e, UT, Rijksmuseum, Mauritshuis, Van Gogh Museum, AMOLF).
- “The painting materials and technique of Van Gogh” (Van Gogh Museum, AMOLF, ETH Zurich, ICN).

Second round 2003- 2008

- “Infrared Reflectography: Evaluative Studies” (RUG, AMOLF, KB, RKD Kroller Muller Museum, American Institute of Conservation).
- “Recipe databases for historical oil painting materials” (ICN, AMOLF).
- “Coordination chemistry of lead carboxylates in aged oil paint films and historically accurate model systems” (UL, AMOLF, ICN, Mauritshuis).
- “The influence of painting methods and materials on the present appearance of 19^{th} century paintings”. (ICN, AMOLF, Van Gogh Museum, Kröller Muller Museum, Courtauld Institute of Art).

Programme De Mayerne symposium

Time	Arrangement	Projects	Title
9.00	Welcome with coffee and tea		
9.30	Introduction Jan Piet Filedt Kok/ Jaap Boon		
9.40	Managing director NWO Leo Coolen		
	Morning chairman: to be announced		
9.50	Leslie Carlyle (P.I.)	Historically accurate reconstructions of oil paint and painting composites	The HART project (page 12)
10.10	Maartje Witlox	idem	Historical Recipe Database-Ground recipes for oil painting: 1600-1900 (page 13)
10.30	Mark Clarke	Recipe databases for historical oil painting materials	Recipe databases for historical oil painting materials: Winsor & Newton Archive (page 14)
10.50	Discussion and comments by AvivaBurnstock		
11.10	Molly Faries (P.I.) and Annelies van Loon	Infrared reflectography: Evaluative studies	Research plan of the project under drawings
11.30	Stephanie Bennet	The painting materials and technique of Van Gogh	unknown
11.50	Beatrice Marino	idem	Imaging analytical studies of grounds used by Van Gogh (page15)
12.10	Discussion and comments by Aviva Burnstock (Stephanie Bennet) and David Saunders (Beatrice Marino and Molly Faries)		
12.40	Lunch break		

Time	Arrangement	Projects	Title
	Afternoon chairman: David Bomford		
13.40	Jaap Boon (P.I.)	Imaging and structural analysis of media and pigments in cross sections of paintings	Imaging analytical studies of paint cross sections (page 16)
13.50	Katrien Keune	idem	How red old master paint transfomrs into black and white (page 17)
14.20	Michiel Verhoeven	Coordination chemistry of lead carboxylates in oil paintings	Deterioration processes in old master piece paintings: Solid-state MAS NMR on paint models and historically accurate reconstructions. (page 18)
14.50	Yoshioko Shimadzu	The influence of painting methods and materials on the present appearance of 19th century paintings	Transparency in 19th century paintings (page 20)
15.10	Discussion and comments by David Saunders		
15.40	Tea break		
16.10	Anne van Grevenstein (P.I)	Comparative studies of paintings in the Oranjezaal	Short introduction
16.15	Lidwien Speleers and Margriet van Eikema Hommes	idem	The Oranjezaal project: evaluation and results (page 21)
16.55	Discussion and comments by Ulrich Schiessl		
17.15	Drinks		
18.30	End		

Abstracts of presentations

Microscopic reseach on Allegory on time, Jacob Jordaens - photo SRAL

The Hart project

Historically accurate reconstructions of oil paint and painting composites

Leslie Carlyle

The Hart (Historically Accurate Reconstructions Techniques) project concentrates on identifying historic recipes for artists' oils, grounds and selected pigments, sourcing contemporary materials which are consistent with those used in the past, then preparing artists'oil painting materials according to representative historic recipes.

The reconstructions which result are used for many purposes: to evaluate historical recipes and their accuracy, to establish studio practices associated with specific materials, and to provide reference materials and standards for instrumental analysis and visual analyses.

As references, reconstructions can be compared visually with actual paint surfaces, to observe gross physical effects (e.g. the effect of adding starch to Lake Pigment), or to compare microscopic cross-sections from both reconstructions and actual paintings.

Oil painting cross sections can tell us a great deal about the materials and application methods used by the artist. Interpretation has been largely based on comparison with samples from other paintings in combination with analyses of the materials present. The Hart project has been preparing historically accurate paints and paint composites to assist this interpretation.

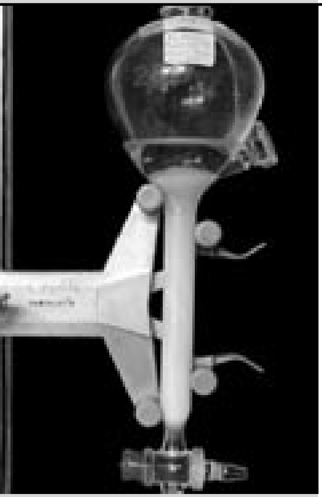
For example, a study of Van Gogh's grounds is underway using this technique. Previous SEM-EDX investigations (Shell/ICN) have provided a comprehensive list of ingredients present in a range of Van Gogh's grounds. However it has been difficult to evaluate the characteristics and proportion of these ingredients present. Therefore a series of paints were prepared with lead white and various sources of two of the common extenders identified: barium sulphate and chalk. Stepped proportions (5%,10%, 15%, 25%, 50%, 75%) were added to lead white and cross sections have been investigated (using SEM-EDX with Kees Mensch and Ralph Haswell at the Shell Research Laboratory). Comparison with an EDX quantification programmes analysing both the reconstructions and the Van Gogh samples has been initiated.

The Hart Project has also been involved with an evaluation of the difference between modern and traditionally manufactured lead white pigment. The traditional material typically exhibits a broad range of particle sizes, from large chunks (10-25 μm) to tiny individual particles (0.1 μm). Whether this resulted from a deliberate mixture of different particle sizes, or is intrinsic to the material was unclear. Reconstructions convincingly demonstrate the answer.

Historical Recipe Database-Ground recipes for oil painting: 1600-1900

Historically accurate reconstructions of oil paint and painting composites

Maartje Witlox



IMAGES Dr. L. Carlyle

Investigations into the history and use of artists' materials naturally rely heavily on historical documentation, primarily recipes. Collecting across countries and centuries allows researchers to evaluate trends and fit observed and analytical knowledge from paintings with contemporary documentary sources.

The first step in creating historically accurate paint reconstructions is to analyse a collection of recipes to establish their relevance, context and the materials required. Consequently, one of the main activities in the Hart Project involves the development of a database to store recipes and to aid in their analysis.

Recipes have been selected according to areas of interest specific to the De Mayerne Programme: lead white pigment, oil processing, driers, preparation layers (grounds) as well as materials specific to Van Gogh's paintings. Recipes originate mainly from Western European countries (The Netherlands, England, Germany, France, Italy and Spain), but recipes from other countries have also been entered to provide a broader context.

At present the collection consists of some 1400 quotes from sources mainly from the 17th to the 19th century. Approximately two thirds of these quotes cover the preparation of materials or paint, but comments on the quality of materials, and on ready-made materials have also been included.

The bulk of time has been devoted to gathering and entering recipes and information. Only recently, in the past six months, it has been possible to make a start with the analysis of these data. The computer program used for collecting quotes has been further adapted to assist in this process. Beginning with preparation layers (grounds), over 250 recipes have been sorted and evaluated according to the materials, and layer compositions. This provides an initial overview of easel painting preparation layers in Western Europe during the 17th to the 19th century. Quotes from the sources not only provide detailed information on materials, but authors also comment on the durability, colour and texture of grounds, the use of absorbent versus non absorbent grounds and on methods of application, etc.

This type of information complements what we learn from the study of actual paintings via cross sections and instrumental analyses. For example cross sections do not often exhibit evidence of size layers- the glue or flour paste used to treat the support prior to the application of the ground. This layer is often very thin, difficult to sample and in the case of canvas paintings, subsequent lining treatments can make identification troublesome. The sizing not only influences the adhesion between support and paint layers, it also can have an effect on the appearance of the paint. The HART Database Project has therefore studied the materials used for sizing layers, collecting and analyzing descriptions of the application process and the frequency with which sizing layers are mentioned or omitted in recipes.

Recipes and information on late nineteenth century preparation layers is being used in the Van Gogh Project to assist with reconstructions of a selection of grounds typical for his paintings.
The Recipe Database is an essential tool for creating historically accurate reconstructions of painting methods and materials. It is intended that this resource will eventually be available to other researchers as well.

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

Recipe databases for historical oil painting materials

Mark Clarke

Digital images of the recipe archive of Winsor & Newton are being captured, and entered into an innovatively structured database. This pilot project will embrace the part of the nineteenth-century archive that deals with oil paint (≈ 5300 pages). This includes detailed recipes for the manufacturing of pigments and media, for mixing tube paint, and for making special equipment. Working notes show, for example, how (and on what date) processes were revised to improve quality, reduce expense, or take account of variability in raw materials. This is the first time this archive has been made available to researchers, and it provides a unique insight into nineteenth century painters' materials.

A new database approach has been developed for making the contents of a documentary source widely accessible without the need for exhaustive transcription or complex editing. The electronic availability of historic recipes greatly facilitates correlation between analytical results and information from documentary sources, thus serving conservators, conservation scientists and art historians. The database displays full page images from the source, alongside an 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 are not restricted to the original interpretation in the entries. Interpretations of the content of the text may be added as required, depending on the interests of an individual researcher.

Another innovative feature of the database is the inclusion of "open fields" which allow future researchers to enter keywords and tag documents in order to carry out searches specific to their own needs.

The database fields include subject classifications, and a summary of the information from each recipe. This allows researchers to search for specific recipes, materials and methods, and to carry out other searches and sorts, e.g. to sort all found results chronologically. Related or cross-referenced records are accessible by clicking a button. In particular all materials mentioned are entered, using both the original wording and also an interpretation of obsolete words, difficult words, code words or abbreviations into modern terminology (e.g. "muriatic acid" = hydrochloric acid.) Recipes are also indexed by quantities and proportions of materials, to enable variations or similarities in preparation to be identified.

The use of page images ensures that indexing is faster than keying in full texts, especially when the texts are hard to read. This is vital if such a large archive — perhaps 20,000 pages when including watercolour recipes and other material — is to be made quickly and comprehensively available. Using images from the original document means that all diagrams, notes, etc. are also available, and, importantly, it allows readers to use their own experience to read passages that might be incomprehensible to the first compiler of the database.

The project started on time, on 5 January 2004, and is progressing well. Six months was allocated for database design, build and evaluation; this was completed on time, and data entry is now underway. Two thirds of photography was completed by March 2004 with further scheduled in August. There are 5300 pages to be indexed in the remaining 18 months of the project. The rate of data entry during July 2004 shows this to be achievable.
As an important deliverable from the De Mayerne Programme, this database will have a lasting impact on the study of art technology.

Imaging analytical studies of grounds used by Van Gogh

The painting materials and technique of Van Gogh

Beatrice Marino

Self-portrait as a painter, Vincent van Gogh, © Van Gogh Museum, Amsterdam

Late in the 19th century, Van Gogh like many painters would buy ready-made artists' materials, including paints and ready-primed supports. It is of interest for conservators and art-historians for dating and technical issues to distinguish the different formulations and different production batches of paints, grounds and supports.

A group of nine paintings of the Paris period by Van Gogh on ready-primed cardboard supports are presently under investigation. Six of the paintings represent a plaster cast model against a blue background and other three are self-portraits.
Previous SEM-EDX investigations on cross-sections from these paintings and visual examinations of the edges of the painted cardboard supports suggest a subdivision of the supports in two groups according to the materials used for the grounds, and that the cardboard supports were cut down from larger sheets.

The main aim of our investigations is to classify the samples in a quantitative fashion in terms of the materials and their distribution in the different recipes of the ground.
Information from various image analytical studies using LM, FTIR, VIS, SIMS, SEM-EDX and Back-Scatter SEM data of cross sections from paintings by Van Gogh provide detailed information on the distribution of the pigment particles and binding medium components in ground and paints.
The imaging techniques were first applied to one of the samples to explore the analytical capabilities offered by the different analytical tools, in order to find critical features and to develop a methodology of classification.

The results obtained to date point at the ground as the most promising basis of classification of the cardboard supports. Differences in the formulations, in terms of composition, proportions and particles size distribution of materials, and the type of binding medium are envisaged as determining properties. Presence or absence of flint particles as well as of biogenic components in chalk are potentially good discriminating features. Elemental maps obtained by SIMS and SEM/EDX provide good data sets for multivariate analytical classification and comparison. The present analytical approaches on the cross sections provide simultaneously detailed information on the paints. This information not only provides more comparative information on Van Gogh's painting materials, but is at the same time a good database for comparison with the materials used by his contemporaries.

Imaging analytical studies of paint cross sections

Imaging and structural analysis of media and pigments in cross sections of paintings

Jaap Boon

The aim of the MOLMAP project is to visualise the atomic and molecular features in the build-up of paint in paintings (the study is supported with one oio position leading to a PhD degree). This goal is mainly achieved by studies of embedded paint cross sections (XS) with imaging analytical techniques that map visual spectroscopic features, UV-fluorescent features, chemical functional group distribution using FTIR and Raman spectroscopy, elemental composition using SEM-EDX and SIMS, and molecular distributions using imaging SIMS. Some of these techniques are novel in the field of art technical studies thus requiring fundamental study of the significance of the molecular and atomic signatures for the understanding of the material consistency of aged paints. The combined images mutually support each other and produce the overall information landscape that can be derived from a paint cross section.

In the last two years we have focussed on the various aspects of oil paints with respect to their speciation in the fatty acid and diacids components as free fatty acids, glycerol ester bound fatty acids and metal carboxylates. Analytical studies of reconstructions, aged reconstructions and XS from paintings from the 15th to 20th century have shown that the ratio of palmitic to stearic acids, which is often used for typing of the original oil or lipids used for binding, can be determined in a spatially resolved way. This study has been submitted for presentation on the ICOMCC-2005 meeting. Studies have been performed that image the azeleic acid distribution using SIMS data of gold coated paint cross sections.

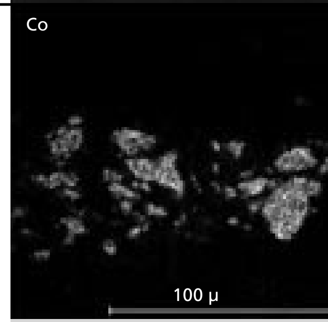
A study of a 15th century paint cross section by Rogier van der Weyden by imaging FTIR, SIMS and SEM-EDX published earlier this year showed that the atomic and molecular distributions observed by the techniques match well (1). Moreover, the fatty acids are clearly present in metal carboxylate form. For the first time, the P/S ratio could be reported for three individual main paint layers analysed in one single measurement. The study to be reported at ICOMCC2005 reports P/S ratios determined on broader range of time scales in the history of painting.

Imaging studies have assisted greatly in understanding the formation of lead soap aggregates in lead-tin yellow paint layers and lead white underpaints, and zinc soap containing 19th C paints. Earlier this year a mechanism was proposed at IRUG-6 in Florence that rationalises the process of formation of lead soap aggregates as the reaction product of poorly formulated lead-tin yellow pigments (2). Lead oxide phases in the original pigment react with free fatty acids that develop as ageing progresses. Depending on the relative distribution of the reactive lead phases in the pigment, the pigment particles remain intact or disintegrate driving the lead-tin yellow residues to the periphery of the growing lead soap aggregate. The evidence for this mechanism using FTIR, SEMEDX and SIMS data will be the central theme of the short presentation during the meeting.

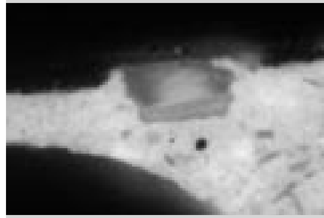
References:

1. Katrien Keune and Jaap J. Boon (2004). Imaging secondary ion mass spectrometry of a paint cross-section taken from an Early Netherlandish painting by Rogier van der Weyden, Anal. Chem. (2004), 76(5), 1374-1385.

2. Jaap J. Boon, Emily Gore, Katrien Keune and Aviva Burnstock (2004). Image analytical studies of lead soap aggregates and their relationship to lead and tin in 15th C lead tin yellow paints from the Sherborne tryptich. In: M.Picollo Proceeding of the 6th IRUG conference, 29 March – 1 April 2004, Florence.



Imaging SIMS shows that Cobalt (Co) remains in the discolored smalt particles in a cross section of a painting by P. Aerts



Paint cross section with a protrusion in the black drapery of Frans Hals' *Portrait of a standing man* (Mauritshuis inv no 928)

How red old master paint transforms into black and white

Imaging and structural analysis of media and pigments in cross sections of paintings

Katrien Keune

Passages of vermilion paint that are part of the early reworking of Peter Paul Rubens' *'Portrait of a Lady'* **exhibit the degradation phenomenon known as blackening vermilion. The current hypothesis on the blackening of vermilion states that meta-cinnabar (black) and calomel (white) are formed at the same time under the conditions of exposure to light and the presence of chlorine (as external source). In a sample taken from the red bow in an area of pure vermilion where a thick crust of darkened material has formed, two degradation products are observed, a black and a white one.**

The total thickness of the vermilion layer is 30 µm and fully two-thirds of that layer is discoloured (20 µm), containing both the black and white products. The vermilion grains are large and coarse and in some instances an individual particle is partially degraded consisting of a black upper part and a red lower part. The large intact and partially degraded pigment particles make this paint cross-section valuable for investigation. The partially degraded vermilion particles indicate the vermilion is altered first into a black product. Because the white particles are found only on the upper surface of the degradation layer – around the dark product – from the vermilion containing paint cross-section questions the current hypothesis. SIMS can detect certain elements with a concentration below the detection limit of EDX. Our SIMS measurements show the presence of chlorine inside the red vermilion while EDX analysis fails to detect chlorine in the same vermilion particle. The chlorine ion yield remains equal or increases in the degraded vermilion compared with the yields in the intact vermilion. Furthermore, the sulfur yield is diminished in the degraded particles compared to the yields in the intact vermilion. EDX analysis showed that sulfur has migrated into the environment outside the vermilion particles.

These results and literature studies lead us to the conclusion that meta-cinnabar cannot have formed. And that chlorine, present as a minor element in the unchanged vermilion, acts as a catalyst and triggers the reaction between vermilion and light to form metallic mercury, which absorbs onto the intact vermilion. This process results in the black product, the first degradation product. After the blackening of vermilion, excess chlorine reacts with the mercury to form the white calomel (Hg_2Cl_2)

Deterioration processes in old master piece paintings: Solid-state MAS NMR on paint models and historically accurate reconstructions

Coordination chemistry of lead carboxylates in oil paintings

Michiel Verhoeven

The formation of postules and protrusions on oil paintings from the 16th -19th century is a serious problem to our cultural heritage. Museums are encountering these protruding defects in a growing number of paintings, to date over 100 Master Piece paintings with such defects have been discovered. The defects dramatically alter the image and hence can hamper the interpretation of these paintings. It is generally accepted that the changes in the surface of the paintings are caused by chemical alterations that occur in the paint film over time. Recently, it has been discovered that the formation of defects is related to the use of certain pigments, in particular Lead White.

Since this pigment is ubiquitously present, it is of utmost importance to reveal the role of this kind of pigment in the formation of defects. As determined with analytical chemical techniques, like GC-MS and IR-imaging in the group of Prof. Dr. J. Boon the protrusions contain high concentrations of lead carboxylates with long saturated alkyl chains *i.e.* lead stearate and palmitate. With the knowledge from modern paint literature the chemical reactions that may cause these deterioration of the paint film have been evaluated. It has been postulated that most probably over time the binding medium and pigments transforms from a (per)oxy linked triglyceride network to a network of ionomers of metals, diacids and non-reactive carboxylates. The latter system is apparently not stable and as a consequence the lead stearate/palmitate fraction separates from the bulk of the paint layer forming accumulations of soapy material.

From the chemists point of view it is important to understand why and how the processes described above are taking place. In other words factors like the thermodynamic stability of the different components and the mechanism and driving force behind accumulation are of interest. To obtain knowledge on the complicated system of pigment and oil degradation products, it is important to first have a thorough knowledge on the separate components.
At the same time it is important to develop model systems that are close to historical paint to be able to draw conclusion that can be extrapolated to historic paintings. The objective of our project was to gain insight in the co-ordination chemistry of the lead carboxylates and carbonates in the processes that are taking place in ageing paint networks. Our approach was to monitor the (changes in) 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. The asset of NMR is that the lead nucleus can be observed directly and in the paint layer. Additionally the response of the NMR signal to changes in the lead environment is known to be very strong.

The first step in this project has been the synthesis and characterisation of a selected library of relevant lead(II) carboxylates and carbonates with solid-state 207 Pb and 13 C NMR. The lead carbonates have proven to be a difficult and complicated multiphase system; synthesis of pure compounds is not straightforward in the pH range relevant for our research. With respect to the NMR experiments on lead carboxylates, we have formulated a qualitative relationship between chemical shift and molecular structure in 207 Pb NMR by using single-crystal X-ray reference data. This correlation is essential to interpret the NMR response of the paint samples in our study.

Subsequently, artificial and historically accurate paint samples have been prepared by or in collaboration with the group of

Background courtesy of Royal Picture Gallery Mauritshuis, The Hague

Dr. L. Carlyle and examined with 207 Pb en 13 C NMR. We observed that especially the 13 C spectra are very indicative for the changes that are taking place in the binding medium. So far this is the first time that paint layers have been investigated with solid-state NMR. The results corroborate previous data on model paint in the literature. Also we observed that in historically accurate paint samples already in first few years the signals of glycerol ester disappear, while at the same time the signal of metal carboxylates increases. These results suggest that the formation of lead carboxylates takes place before accumulation starts. In conclusion: to make a substantial contribution to the field of art history and restoration more (solid-state based) chemistry oriented research is necessary.

Fundamental understanding of the processes that take place during postule formation and subsequent protrusion demand a profound description and understanding of the various system components both pigments and aged paint. Also the interaction of pigments with long chain acids and esters needs further investigation. The chemical composition and prerequisites of the soap formation and accumulation should be studied in detail under model conditions with recent insights from the group of Dr. L. Carlyle about artificially generating protrusions.

Transparency in 19th century paintings

The influence of painting methods and materials on the present appearance of 19th century paintings

Yoshiko Shimadzu

Many oil paintings of the 19th century show severe paint defects such as drying cracking (aligatoring), changed transparency, darkening, opalescent gelification, blanching, and colour changes. These alterations seriously affect their appearances, diminish their aesthetic quality and could distort art historical interpretation of the painter's intent.

Changes in transparency will lead to underlying paint layers becoming more or less visible, changing the appearance of the paintings. Our research focus is especially on transparency changes in relation to darkening, since this phenomenon occurs in several 19th century paintings in Dutch collections*. In previous research of the painting by Th. Rousseau, and F. Verster, their darkening seems to be related to yellowing of medium.
Factors which may cause changes in transparency of medium are defects of the applied material itself, synergism due to the mixture of at least two materials, and the effect of additives such as dryers. Since the working methods, techniques and materials used by artists changed drastically during the 19th century, association with used materials, preparation methods of materials, and artists' techniques should also be considered.

How to evaluate the appearances of paintings

The appearance of a painting is determined by a very complex set of factors, since the painting is consisted with ground layer, paint layer(s) and mostly varnish layers. Each layer has its own light scattering and absorption. If the thicknesses and degrees of gloss, scattering and transmission of each layer are measurable, optical evaluation and comparison could be possible. In addition, the condition of the surface plays a role. To study changed appearances of paintings, evaluation methods and objective indices are required. To unravel the different factors involved, we plan to focus on the study of transparency changes in simple, one or two layer systems, employing materials that were found in 19th Century paintings studied previously.

Research plans for next year

1. reading bibliographies (optical measurements and theories including Kubelka-Munk theory and writing an introduction to this topic, artists' techniques in 19th century, previous research of appearance changes; pigment alteration, yellowing of oils and so on),
2. planning and preparing a discussion meeting on transparency and/or its changes in paintings,
3. selecting methods and materials for reconstructions of oil paint films, in co-operation with Dr. Leslie Carlyle. We are planning to carry out small experiments using white lead with oil. The effect of lead dryers would be included in our reconstructions, since it seems to have a effect on transparency and perhaps yellowing of the medium,
4. studying actual oil painting by Th. Rousseau which has already changed transparency,
5. taking courses on how to apply analytical equipments (colour meter, microscope, etc.) to oil paint samples.

*K.J. van den Berg, M. Geldof, S. de Groot and H. van Keulen. 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.

The Oranjezaal project: evaluation and results

Comparative studies of paintings in the Oranjezaal

Lidwien Speleers en Margriet van Eikema Hommes

The ensemble of 44 allegorical paintings in the Oranjezaal was painted between 1648 and 1652 by twelve famous artists from the Northern and Southern Netherlands. To establish the required unity in the ensemble, painters were sent pre-grounded canvases and instructions on measurements, composition, perspective and direction of light to be depicted. This uniformity in commission, together with the good condition of the paintings and their similar well-documented history, offered a unique possibility to compare and to correlate the materials, techniques and style of the individual painters.

In this lecture, some of the most important results of the comparative studies will be presented.

The research has given much insight into the divergent methods that existed in the 17^{th} century for underpainting and how in the subsequent paint layers artists varied their paint application (i.e. for example, the way the underpaint was left visible, differences in consistency of the paint and the rendering of contours) in order to achieve a convincing modelling of the individual figures and a convincing spatial illusion in the representation as a whole. Furthermore it has shed light on the frequency of use of known and less well-known painting materials.

The newly gained knowledge of the individual methods of the painters has resulted in new attributions for some paintings. It also made it possible to distinguish different hands in one painting, especially in the paintings of Van Honthorst and Van Campen, which has yielded more insight on the division of labour in their studios.

The examination of the paintings combined with historic documents related to the decoration of the hall, and other 17^{th}-century sources also shed new light on the pictorial concept of the hall as a whole. It appeared that the decoration may be interpreted as one large trompe l'oeil of the arches used in contemporary triumphal processions. It also appeared that in this concept the rendering of different types of day light played an important role.

One of the most unexpected results of our research was that marked differences existed in both technique and style between the paintings of one artist. Several painters, for example, differed their type of underpainting (monochrome or coloured, transparent or applied as a covering layer etc), use of contours, and brushwork. Their choices were based on, the subject depicted, the height in which the painting was to hang in the hall, and, interestingly, also on what type of light they were to depict in their paintings. This flexibility of artists in choosing their painting methods in relation to the specific painterly goal they had in mind, has until now received hardly any attention in art historical studies.

Thomas Willeboirts Bosschaert, detail from Frederik Hendrik and Maurits as commanders, with in the distance the battle at Nieuwpoort, ca. 1650 *photo SRAL*

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RUG (University of Groningen)
SRAL (Limburg Conservation Institute)
TU/e (Technical University Eindhoven)
UL (Leiden University)
UT (University of Twente)
Van Gogh Museum

Collaborating institutions

American Institute for Conservation (AIC)
Cambridge University
Chicago Institute of Art
Courtauld Institute of Art
ETH (Swiss Federal Institute of Technology)
Hamilton Kerr Institute
Imperial College London
Kröller Müller Museum
KSLA (Royal Dutch Shell Research Laboratory
Laboratoire de recherche des musées de France
Musée d´Orsay
National Gallery, London
National Gallery of Washington
RKD (Netherlands Institute for Art History)
Tate Gallery
UvA (University of Amsterdam)
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