The "De Mayerne program"

A research program on Molecular studies in Conservation and Technical Studies in Art History

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.

October 10th, 2000

Contents

Annexes

1. Introduction

The NWO Priority Program MOLART -- *Molecular Aspects of Ageing in Art* (1995 - 2001) -- has been acting as a catalyst to bring together members of the research community on technical studies in art history, molecular sciences and conservation in the Netherlands. MOLART has been a recognisance program on molecular studies of art objects especially paintings. It has 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. New molecular level information was obtained that elucidates processes of chemical change in the natural products used as binding media, varnishes and in photo-chemically sensitive pigments. Historical studies of painting materials and painting methods revealed new information sources suggesting hitherto unknown paint material preparation techniques. MOLART has opened up the multidisciplinary field of molecular studies of paintings and their conservation.

The De Mayerne program[1] has the ambition to further develop and extend the knowledge and insights on molecular and paint technical structure of paintings obtained in the MOLART-project. The mission of the De Mayerne program is to establish a strong cross-disciplinary central research program 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 program 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 will be given to the multidisciplinarity of the projects and their application in art history, art chemistry and in conservation practice.

The research on the paintings ensemble in the Oranjezaal of the Royal Palace Huis ten Bosch, offers a unique chance to examine and restore a collection of paintings, which have been kept under known circumstances in one room for over 350 years. This research was started already during the MOLART-project and offers a wealth of information on the making of the paintings and on the painters themselves. These studies, studies of works by the same painters displayed in museums and comparative studies of other 17th C paintings will provide the basis for a handbook on the painting technique and the studio practice in the Dutch Golden Age.

The information gained from the De Mayerne program is not only of interest for a select group of researchers, but will also contribute to the dissemination of art historical and technical aspects of paintings to the public at large via exhibitions, publications, educational activities etc. The close collaboration and feed-back from Dutch museums is therefore regarded as essential to the success of the De Mayerne program, an engagement that furthermore guarantees a broad relevance of the mission. Interdisciplinary co-operation between the disciplines art history, conservation and natural sciences will - as a follow up of the MOLART-project - lead to the development of a new generation of art historians and physicists and chemists that consider this collaboration a natural process. This collaborative effort should provide new insights and knowledge relevant for all participating disciplines.

---

[1]This program proposal was prepared by dr. K.J. van den Berg, prof.dr. J.J. Boon, dr. L. Carlyle, drs. R.J. Hoppenbrouwers, prof.dr. M. Faries and dr. A. Wallert, in cooperation with dr. J.P. Filedt Kok and dr. N.J. Kos.

The underlying program presents research topics of great interest for the various disciplines. Short descriptions presenting the rationale for the research proposed are presented in annex 1. A large number of institutions with an interest in the preservation of our cultural heritage have been brought together. Several institutions abroad have expressed an interest to collaborate. The research topics have been grouped together to form multidisciplinary project clusters to optimise the collaborative effort and insure a responsible and optimised interpretation of the results.

2. Research program and project clusters

The De Mayerne research program relies strongly on studies in historical art techniques and materials, which utilise the material properties of the art, object as a source of information on medium use and artistic intentions of the painter. Technical studies of art aim to explore the physical reality of paintings by the direct analysis of works of art with sophisticated technical means. The results supported by studies of artist manuals and other written sources provide insight into the history of materials and methods of the use of painting materials. Thus, attempts are made to construct narratives of artistic production and subsequent survival and change. The application of new methodologies and the performance of fundamental studies in a close collaboration with chemists and physicists make unique contributions to the field and improves our interpretation of paintings. It is in this context especially important to have access to new techniques that provide insight on the molecular level. It is becoming possible to examine the composition and distribution of inorganic and organic components with a high resolution by the linking of microscopy, spectroscopy, mass spectrometry and advanced data processing methods. New theoretical insights in chemistry and physics can be applied to the complex chemical and physical interactions of the many components of paintings, the interfacial interactions between the paint particles and binding media in the multilayer structure and the processes of change due to ageing of the materials.

In order to interpret a painting from the point of view of an art historian, conservator, curator and even the general public, we have to understand what influences change in painting materials. Changes in the optical appearance, surface characteristics and the development of certain paint defects, affect the meaning, aesthetic quality and long-term stability of the works of art. This research program proposes in-depth studies to understand fundamental aspects of these changes in appearance. Image plane studies, the chemistry in the layer structure of the painting, reconstruction of the paint materials and the paint layer structure, and the effects of restoration and conservation, provide information that allows a better interpretation of the present state of the image. This information is imperative for the protection and long term preservation of our cultural heritage.

The program proposes to investigate paintings in an interdisciplinary setting from the 15th and 16th century, the Dutch Golden Age, the 19th century, and illuminated western and non-western manuscripts. The methodology consists of the observation of technique and condition, obtained with traditional and more advanced scientific methods pieced together with information on historic technologies, workshop practices, patrons and provenance. The focus of this research is artistic intention and how it is changed by molecular changes due to changes in co-ordination chemistry, photo- and autooxidation, cross-linking, hydrolysis, acidification, solvent leaching etc., causing physical changes in appearance observed as fading, discoloration, darkening, deformation, cracking, increased transparency, efflorescence and blooming.

Following the previously approved research program (MOLART II dd. 12.I. 2000) multidisciplinary projects have been developed that group research topics together in project clusters in which research groups from different institutions collaborate. The project clusters are also the anchors for the general call for proposals. In competition, project cluster proposals will be selected to be financed under the program. Each project cluster is co-ordinated by a co-ordinating principal investigator (CPI). The added value of this approach is the strengthening of the multidisciplinary collaboration. The following project clusters have been developed in the context of the De Mayerne program:

PROJECT CLUSTER	Co-ordinating PI
P 1: Comparative studies of the paintings in the Oranjezaal	A. van Grevenstein
P 2: Painting technique and the studio practice in the Dutch Golden Age	Dr. A. Wallert
P 3: Co-ordination chemical changes in oil paintings	Dr. J. Haasnoot
P 4: Imaging microscopy of paintings cross sections	Prof. Dr. J.J. Boon
P 5: Reconstructing 17^{th} and 19^{th} C oil paint	Dr. L. Carlyle
P 6: Painting media of Van Gogh	E. Hendriks
P 7: Effects of cleaning	A. van Grevenstein
P 8: High resolution IRR studies paintings and miniatures	Prof. Dr. M. Faries
P 9: 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	IJ. Hummelen

The following short abstracts of these project clusters are intended to get a first impression. The role of the CPI will be to co-ordinate the development of the full project cluster proposal once the call for proposals has been launched. Each multidisciplinary cluster addresses a number of the topics mentioned in annex 1: the numbers refer to the short descriptions in this annex. The institutions participating in each cluster are listed.

P1: Comparative studies of the paintings ensemble in the Oranjezaal of the Royal Palace Huis ten Bosch

CPI: van Grevenstein (SRAL, Stichting Restauratie Atelier Limburg, Maastricht).
Collaborating institutions: SRAL, AMOLF, RUGroningen
This project cluster involves topics: A1a, D1a, D2a (see annex 1)

The Oranjezaal in the Royal Palace Huis ten Bosch holds a large scale paintings ensemble in pristine condition painted by famous artists from the Republic and Southern Netherlands. The proposed project presents an unusual opportunity to study paintings in their “original” state and to compare making of these paintings with other 17^{th} C paintings with a complex history.
All the paintings of the ensemble were made within the rather strict confinements and demands of the architecture. While such conditions were very similar, the paintings of the ensemble are strikingly different in style. This raises many questions about the relationship between style and technique (see A1a). The paintings furthermore provide the opportunity to do comparative studies on other paintings commissioned in the public domain by the same painters that have experienced entirely different preservation conditions. This project is part of a more extensive research project co-ordinated by SRAL on technical and conservation studies of the Oranjezaal ensemble. Due to a very tight schedule, microscopic (D1a) and IRR studies (D2a) have started in collaboration with MOLART and the RUGroningen in 2000 and are proposed to continue in the De Mayerne program till 2003.

P2: Painting technique and the studio practice in the Dutch Golden Age

CPI: Wallert (Rijksmuseum)
Collaborating institutions: Rijksmuseum, Mauritshuis, AMOLF, RUGroningen, UvAmsterdam, RKD
This project cluster involves topics: A1b&c, D1a&b, D2a, D2c (see annex 1)

An important stylistic shift resulting from artistic and economic competition took place in the second and third decades of the seventeenth century. By the 1640s Amsterdam had taken over the position of Antwerp as the foremost staple market for pigments, organic dyestuffs and other paint materials. These developments must have affected the choice and qualities of the painters materials, as well as the way these materials were applied as will be examined in a number of representative paintings from collections in the Rijksmuseum and the Mauritshuis (see A1b). In this context various problems of seventeenth century paint formulation will be addressed using advanced microscopic-spectroscopic atomic and molecular imaging techniques and mass spectrometry at AMOLF and XRD at the UvAmsterdam (see D1a&b). Classicist painting later in the century, largely driven by art-theoretical considerations, was done with different use of materials. The technical peculiarities of this extremely important art historical development have hardly ever been the subject of investigation. The materials and methods of application will be studied in the works of classicist painter Gerard de Lairesse and other painters of decorative ensembles like Hondecoeter, Glauber, and de Wit (see A1c). High resolution XRF will be applied to map the distribution of pigments directly on the painting (D2c) to avoid sampling.

P3: Co-ordination chemical changes in ageing oil paintings

CPI: Haasnoot (ULeiden)
Collaborating institutions: ULeiden, AMOLF, Rijksmuseum, Mauritshuis, ICN (Instituut collectie Nederland, Amsterdam), SRAL
This project cluster involves topics: B1, D1a&b, B3, C1, A 1-A3 (see annex 1)

This project concerns theoretical and experimental studies of the co-ordination chemistry in paint layers to explain changes in the paint chemistry of ageing paintings (see B1). On the basis of the results gained by the analytical work that has been done and is being done by MOLART, it is proposed to perform fundamental studies on the behaviour of metals like lead, copper, cobalt, manganese, iron and etc. in their complex reactions with the constituents of paints. This study is of great relevance for a better understanding of the behaviour of lead white, smalt, azurite, Sienna and omber in ageing oil paint. The influence of simple co-ordinating groups and anions like fatty acids and diacids, terpenoid acid and hydroxy groups, chloride, sulphate, carbonate, acetate and potassium (from smalt) on the stability of ionomeric oil paint will be studied. The rationale for this fundamental work is provided by observations on paint composition using the advanced spatially resolved imaging of samples from paintings using imaging SIMS, HR-SEM and FTIR at AMOLF linking this project to A1, A2, A3 and D1a. Co-ordination chemical aspects of traditional paints also play a role in the cleaning of paintings (see C1) and the effects of the chemical atmosphere around art (C2). Attention will be given to the problems of changes in transparency and lead white diseases with a particular emphasis on lead compounds, which are one of the most ubiquitous substances in traditional painting (see B3).

P4: Imaging microscopy of paintings cross sections

CPI: Boon (AMOLF)
Institutions: AMOLF, Rijksmuseum, Mauritshuis, Van Gogh Museum, SRAL, ICN, Tate Gallery
This project cluster involves topics: D1, A1-A4, B1, B2, B3, C1, C2 (see annex 1)

The microscopic-spectroscopic and microscopic-mass spectrometric examination of cross sections is of vital importance for technical studies in art history, studies of processes of chemical change in paintings and effects of conservation methods. New instrumentation available at AMOLF (Imaging SIMS, HR-SEM-EDX and organic molecule microscopy) makes it possible to derive the binding medium composition and distribution between organic and inorganic components in painting cross sections with a resolution within one micron. This opens unique possibilities to re-examine the technique of van Eijk and other early oil painters (A3), to perform comparative work on the Oranjezaal and other painters of the 17th C (A1) and to assist in detailed studies of Van Gogh and his contemporaries (A2). The methodology is especially suitable for fundamental studies of the instability of certain pigments such as smalt (Co-glas), orpiment and copper glazes (A1), and the effect of chlorine and other impurities in lead white (A1 and B3). Imaging SIMS and FTIR will be applied to improve our understanding of the phenomena due to disruption of the ionomeric network in paintings (B1, C1,C2). The research team in this cluster will focus on facilitating the application of the instrumentation to paintings cross sections, which will require finding solutions to the many complications imposed by such samples from paintings and model systems. A very close collaboration is envisaged with the art chemists and technical art historians in other project clusters (P1, P2, P3, P5, P6, P7, P9 and P10).

P5: Reconstructing 17th and 19th C oil paint

CPI: Carlyle (ICN)
Collaborating institutions: ICN, TUEindhoven, TUTwente, Rijksmuseum, Mauritshuis, Van Gogh Museum, AMOLF
This project cluster involves topics: B3, A1-3, B4, D1b (see annex 1)

The consistency and properties of oil paint of traditional paints prepared according to historical sources is the focal point of this project cluster. Paint is prepared in workshops (17th C) or by specialised colormen (19th C). This paint is however modified by the artist and by its way of application in the multilayer paint system. So the reconstruction implies not only methodology of paint preparation but also of paint use in artistic practice. The chemical and physical properties of the paint during preparation, application, in the early stages of drying and after a certain period of ageing are the focus of the research. Observed paint defects in paintings from the 16th to 20th C will be studied using the experimental approach of historically correct reconstructions. Special attention will be given to lead white paint, the problem of increased transparency and lead white diseases (see B3). The availability of the MOLART Ageing facilities for paintings at SRAL is essential for this project.

P6: Painting media of Van Gogh

CPI Hendriks (Van Gogh Museum)
Collaborating institutions: Van Gogh Museum, AMOLF, ETH Zürich, ICN
This project cluster involves topics: A2b, D1a&b, B3, A2a (see annex 1)

A lot is known about the painter Van Gogh and his oeuvre but many questions remain about the composition of his painting materials and their long term ageing behaviour. Samples from paintings, palettes and original tube paints are available for this project. How did Van Gogh influence the rheology of his paints? What is the condition of the paint surface and can we restore the original condition of the paint surface? What is the chemical condition of the proteinaceous varnishes? Can we use the trace element composition and other features of his paints for authentication? These and other questions will be addressed in this project cluster using several advanced microscopic techniques at AMOLF and ETH in Zürich (see A2b). General questions concerning contemporaries of Van Gogh are embedded in other projects running at ICN and P5.

P7: Effects of cleaning

CPI: A. van Grevenstein (SRAL)
Collaborating institutions: ICN, SRAL, ULeiden, AMOLF
This project cluster involves topics: C1, B1, D1a&b, A1-3 (see annex 1)

Cleaning is one of the most frequently recurring tasks of maintenance of optical and aesthetic quality of paintings. Questions remain on the exact details of the effect of aqueous and non-aqueous cleaning on the paint surface and deeper layers. These effects can now be interpreted as affecting the co-ordination chemistry of the ionomeric network of the paint, which can cause permanent chemical and physical damage. This project cluster will rely strongly on the fundamental research of P3, but focuses on the practical aspects of cleaning using model systems and paintings.

P8: High resolution IRR studies of paintings and miniatures

CPI: Faries (RUGroningen)
Collaborating institutions: RUGroningen, RKD, SRAL, Rijksmuseum, Mauritshuis, AMOLF
This project cluster involves topics: D2a, A1-4, D1a (see annex 1)

High-resolution Infrared-reflectography (IRR) studies provide critical information about the painting process, artistic production, and artistic intention; it therefore enlarges the possibilities for the integration of various types of material data. MOLART has been the developmental phase of the advanced AIM PtSi 540 x 486 IR focal plane camera, and it is proposed that the De Mayerne program will support a phase of implementation and further evaluation. D2a shortly summarises these plans in more detail. Interactive research is proposed in paintings studies described in A1-A3 where the instrumentation is used as lead-in research. Feasibility studies are planned on miniatures (as presented in A4), which offers the unique opportunity to apply this advanced methodology for the first time. Analytical support using advanced microscopy-spectroscopy will be provided though D1.

P9: Fate of proteins in works of art

CPI: Boon (AMOLF)
Collaborating institutions: AMOLF, UUtrecht, CCI Ottawa, Rijksmuseum, Mauritshuis, Van Gogh Museum
This project cluster involves topics: B2, D1 a&b, A1-4 (see annex 1)

Recent advances in biological mass spectrometry have made it possible to open an analytical window on proteinaceous substances in art that goes beyond amino acid analysis. Proteinaceous materials are present in many different ways in paintings: as paint binders in egg tempera and in the under-painting of oil paintings, as intermediate layers within the oil paint composite, as egg white varnish, as canvas sizing-glue, as glue layers between layers of ground, as component in lining glue (see B2). For this reason, there are strong links with the painting research in A1-4. It is proposed to develop methodology to directly identify proteins by microscopy-MS techniques in the cross-sections (see D1a and A3) and BIOMS techniques (D1b). Proteins undergo many chemical and physical changes, depending on the structure of the constituent amino acids, that can be studied with mass spectrometry. Understanding of the properties of protein networks and especially the role of metals released from pigments in their formation and degradation is of vital importance for a better management of paintings and other art objects, where proteinaceous materials have been used. It is proposed to study the chemical changes in proteins due to a paint matrix (protein, oil/protein or protein varnish) in high detail, because more oxidised proteins will react differently to cleaning and preservation treatments. The accompanying changes in physical properties will be studied as part of collaborative research at CCI.

P10: The chemical atmosphere around art: a study of the effects of NOx and related oxidants

CPI: Elsevier (UvAmsterdam)
Collaborating institutions: UvAmsterdam, AMOLF, Rijksmuseum, Van Gogh Museum, Mauritshuis, SRAL, ICN, CCI Ottawa, Getty Museum.
This project cluster involves topics: C2, D1a&b (see annex 1)

NOx are extremely dangerous for works of art because of induced autooxidation under dim light conditions, formation of nitrite salts with metals from pigments, titration of the ionomeric oil paint network due to acidification and the destruction of the support. The focus of this project cluster is to obtain more fundamental understanding of the mechanism and to develop methods to prevent its destructive activity. Part of this project will be to evaluate the pros and cons of complete anoxic enclosure of paintings.

P11: Surface studies of paintings by UV-VIS

CPI: Hummelen (ICN)
Collaborating institutions: ICN, Rijksmuseum, Mauritshuis, Van Gogh Museum
This project cluster involves topics: D2 b, A1b, A2, B3 (see annex 1)

Objective colour registration is a first condition for the accurate evaluation of the effects of change, like darkening, discoloration, increased transparency, cracking and cupping, on the appearance of the painting. Accurate detection of these effects by a high resolution (spatial and colour) camera will be employed for monitoring and for the evaluation of the impact of these changes on the appearance of the painting, for colour analyses and for the evaluation of restoration procedures. Work will include further development of imaging techniques and imaging analyses, protocols (calibration) based on previous results from EC projects like VASARI and MARC.

3. Budget and Organisation

Based on the clusters described in the previous chapter, the costs of the program can be estimated as follows. This budget does not include several projects that will be submitted for granting elsewhere, e.g. to the STW. It also does not include large investments (see annex 1: D.2.).

Ph. D. positions	11 positions	kf 3.300
post docs	15 man years	kf 1.650
senior post docs	5 man years	kf 800
technicians	11 man years	kf 990
fellowships		kf 100
central ageing facility	4 years	kf 90
publications and printing costs		kf 50
travel and conferences		kf 100
secretariat		kf 200
reservation for unemployment costs		P.M.
Total		**kf 7.280**

Although the project clusters are only a minimalist approach to the execution of the program in view of the budget limitations, these together already go well beyond the budget of 4.5 million guilders reserved for the program by the NWO-councils.

Each application can be up to a maximum of 1.0 million guilders. Provided the quality of the proposals is judged sufficiently high, at least four, preferably five project clusters should be granted in a first round of applications, to provide a program of appropriate impact. It is estimated that a budget of approximately 4 million guilders is needed for this first round, based on the clusters given above. It is recommended to establish the deadline for this round no later then March 2001 in order not to lose the momentum of the MOLART program.

A second round of applications should follow around a year later. In this round, which should be open to all researchers eligible for NWO-support, the program can be broadened with new themes, in competition with clusters that were not granted in the first round. A minimum budget for this round should be approx. 2.5 million guilders. The Program Committee should also try to obtain additional external funding for this second round.

A Program Committee established by NWO, will be responsible for the program and the scientific co-ordination, supervised by a small “Steering Committee”. Task descriptions are given in the annex 2.

The co-ordinating principal investigators will be responsible for the budget of the cluster and the execution of the research program. They will also take care of the bilateral contacts with other relevant clusters. They will provide the contributions to the annual scientific and financial report, according to the format provided by the Program Committee. Besides the usual meetings of each cluster, there will be regular (twice a year) meetings of all co-ordinating principal investigators and a yearly De Mayerne day for all involved researchers.

A co-ordinating core group of experts will be appointed by the Program Committee from the co-ordinating principal investigators consisting of an art historian/conservation scientist, historical materials researcher/conservator and a painting material chemist. This core group, assisted by the program secretary, will be given the responsibility for the organisation of the meetings of the co-ordinating principal investigators, the regular progress report meetings with members of the conservators community in the Netherlands and the yearly De Mayerne day for all participants in the program. They will also take care of the final editing of the annual reports.

Applications should focus on the clusters as given above. In each proposal the long-term objectives should be defined clearly. The proposals will be evaluated by an international refereeing process. The judgement criteria for this competition are given in the annex 3.

Applications can be submitted only by multidisciplinary teams of researchers. The Program Committee can give indications for co-operation. Applications can be submitted by staff members with a permanent position, working at universities or NWO/FOM-institutes. Staff members of other non-university institutions, having an independent, non-profit research task, can apply in collaboration with a university or NWO/FOM-institute.

Subsidy can be requested for direct costs of new, temporary personnel (Ph.D. students, post-docs and, by exception, technicians) and related material costs (travel, equipment). The maximum duration of a project is four years. Participating institutions are expected to contribute to the program too, including the work of permanent staff and the infrastructure. To avoid a large reservation for unemployment allowances the applicants are requested to give an indication of the job perspectives for the temporary personnel and - if possible - provide guarantees.

4. Participating institutions and supporting facilities

The main museum research partner in the Netherlands is the Rijksmuseum, which provides 50% of the salary of the art historian in the co-ordinating core group, the involvement of the director of collections as chairman of the Program Committee and the involvement of conservators in the projects (approx. 0.7 fte).

The Mauritshuis will collaborate in restoration projects of 17th century paintings.

The Vincent van Gogh museum will collaborate in research and restoration projects of 19th century paintings.

Other museums that have affinity to the research questions can participate via the regular meetings with curators and conservators or via bilateral contacts.

Also the Rijksbureau voor Kunsthistorische Documentatie, Den Haag will be involved in the program and provides collaboration in the research on 17th century paintings and in the infrared investigations.

The implementation of several of the projects depends strongly on the participation of institutes as Instituut Collectie Nederland, Amsterdam and Stichting Restauratie Atelier Limburg, Maastricht.

Stichting Restauratie Atelier Limburg will provide access to their conservation projects, to facilities for the production of historically accurate reconstructions of paint composites and facilities for artificial ageing of reconstructed paintings and painting materials. SRAL will play an important role in the knowledge transfer.

ICN provides support by providing their expertise and instrumental facilities, including SEM-EDX and CCD-camera, for paintings studies in the De Mayerne Program. Staff members will participate to a maximum of 4.5 fte in a number of projects and will facilitate knowledge transfer.

Participating universities, which will provide the expertise of their staff and their facilities are Universiteit van Amsterdam, Universiteit Leiden, Rijksuniversiteit Groningen en Technische Universiteit Eindhoven.

FOM/AMOLF provides support to use the expertise and instrumental facilities in the Research Program of Macromolecular Mass Spectrometry for the De Mayerne Program, including the painting materials chemist for the co-ordinating group and a technician up to a maximum of 500 kf/year for 5 years. Instrumental facilities include a variety of mass spectrometric and imaging techniques (DTMSMS, PyGCMS, MALDI-TOFMSMS, ESI-FTMS, microscopy LDMS, imaging SIMS, HR SEM-EDX, imaging FTIR, imaging UV-VIS).

An overview of available facilities is given in annex 4.

5. Knowledge transfer and educational objectives

Technical studies in art history have been ongoing for several decades in the Netherlands, but conservation science on an academic level is in its infancy. There are presently very few academic chairs in either area. We hope that the special chair in the Chemistry of Conservation at the Chemistry Faculty of the University of Amsterdam will produce a strong academic research group. SRAL in Maastricht has successfully supported several five-year educational programs introducing its conservation graduate students to various aspects of art history, technical studies, and conservation. Drs. E. Hermens, as guest lecturer, teaches a course on technical aspects of traditional painting methods for art historians of the University of Utrecht and Leiden. Prof. dr. M. Faries, Chair of Scientific Examination of Art (Universiteit Groningen), teaches an introductory, first-year course on technical studies as well as an advanced course which emphasises infrared reflectography (IRR) and the implications of IRR findings for art history. Several universities incorporate material related to conservation and painting technique in classes, but this is not part of a developed curriculum.

This situation contrasts strongly with many other European countries and the USA. On the European level there are many universities that teach Conservation Science and there are several initiatives to come to a European graduate program between several universities in Italy, Spain, Germany and Sweden. There are several universities in the UK where conservation science is being taught (Salford, Glasgow, Cambridge, London). The Courtauld Institute of Art as part of the University of London system has been the cradle of many academic level conservators. The Winterthur Institute (University of Delaware) and the Conservation Institute of Fine Arts in New York are such a center in the USA.

The program may play a supporting role in the development of a graduate level course on technical studies in art history and molecular conservation science by the various academic staff members and interested other parties involved in the project. This course should be meant to introduce science and art history undergraduate students into the specific aspects of the chemistry and physics of museum objects as a foundation for further graduate studies in molecular conservation science and technical studies in art history. Such a course could be an important element in the knowledge transfer and should be accessible for students of all Dutch universities.

The co-ordinating group will be responsible the organisation of regular work group meetings of the De Mayerne Program research project teams, the production of a yearly report and the organisation of regular progress report meetings with members of the conservators community in the Netherlands.

Besides the regular meetings of all researchers participating in the De Mayerne program, quarterly meetings will be organized of the Workgroup Museum Restaurators under the aegis of SRAL and ICN, during which results of the program will be presented and specific problems arising from conservation practice will be discussed. These consultations will also include the specific contributions of the conservation studios to the topics, mentioned under Technical studies of paintings (see annex 1.A), especially concerning current conservation projects.

The researchers working under the De Mayerne program will report regularly on the progress through lectures and participation in (international) congresses. In close collaboration with the practitioners in the field workshops, colloquia and/or symposia will be organised on specific topics.

For the interactive archiving of the scientific data the De Mayerne program will provide access to its analytical microscopy imaging data and image surface data of paintings to the project in Amsterdam aiming at the development of a virtual laboratory.

Besides the annual report the web site of the De Mayerne will provide an up to date review of the current projects, the results, the publications, the lectures and the other activities. This web site should play an important role in the interaction inside the project and with the outside professional world. Possibly the Chemiewinkel Amsterdam is willing to assist in the dissemination of the results.

The results of all projects will be made public in publications for the international professional world, in articles, books or in electronic publications. The Ph.D. students working under the De Mayerne program will of course present their part in the research as a dissertation too. A uniform series of publications, as appears in the MOLART-project, will be considered.

The newly established journal Artmatters that will appear yearly from 2001 can play an important role in the publication of technical studies in art history.

The results will be made accessible for the general public in collaboration with the museums by means of presentations, exhibitions and publications. This can be done in relation to more specific conservation projects. In this scheme the planned publication on the conservation and the research of the paintings in the Oranjezaal in 2003 can be of great importance. This may include smaller presentations and publications concerning the conservation of one or more of the involved paintings in the participating museums. Furthermore the results of the research will be presented in catalogues and other publications on the investigated paintings. The publication of a book on Dutch 17th century painting technique and studio practices in combination with an exhibition of studio presentations (The Praise of the Art of Painting) planned in the Rijksmuseum should be a worthy conclusion of the De Mayerne program.

6. International collaborative links

MOLART has already linked AMOLF, the Scientific Department of the National Gallery of Art in Washington, the Art Historical Institute of the University of Amsterdam, the Scientific Department of the Tate Gallery of London, ICN, SRAL and several museums (mainly Rijksmuseum, Mauritshuis, Van Gogh Museum). Advisory support was given by Shell SRTCA and Akzo Nobel ARC.

In this program a new group of collaborating parties is envisaged, which will consist of University research groups, research groups in academic or government institutions, museums and conservation teaching institutions. There are indications that Akzo Nobel will support the program with expert advice, when requested. There is great interest in the UK (Tate Gallery, Courtauld), Canada (CCI, Canadian Conservation Institute), the USA (GCI, Getty Conservation Institute), Germany (Doerner Institute) and Portugal (Lisbon University, Dept of Chem.; Unit of photochemistry) to collaborate. The links with industry will be strengthened further, especially in view of their contributions in the use of research facilities

Annex 1

Research topics in the De Mayerne program

The research topics recommended for implementation in the De Mayerne program are arranged in accordance with the proposal for the research plan MOLART II (dd. 12.I. 2000) approved by NWO.

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.

As indicated in chapter 2 the project clusters provide a multidisciplinary approach to the topics of the research program. In the following scheme the topics which are elaborated in this annex 1 are ordered according to the objects under study and the focus of the research.

Objects: **Focus:**	15-17th C Painting	17th & 18th Painting	19th and 20th Painting	Miniatures
Painting and Production Technique	A3a van Eijk etc A3b Tempera/oil B2 Proteins D1a Microscopy D1b MS D2a IRR	A1a Oranjezaal A1b Studio practice A1c Classicists B1 Ionomers B3 Reconstructions D1a Microscopy D1b MS D2a IRR D2c XRF D2b UV-VIS	A2b Van Gogh etc A2a Paint B2 Proteins B3 Reconstructions D1a Microscopy D1b MS D2c XRF D2b UV-VIS	A4 B2 Proteins D1a Microscopy D2a IRR
Ageing phenomena	B1 Ionomers B2 Protein D1 Microscopy	B1 Ionomers B2 Protein D1 Microscopy	B1 Ionomers B2 Protein varnish B3 Reconstructions B4 Mechanics D1 Microscopy	B2 Protein D1 Microscopy
Preservation	C2 NOx	C2 NOx	C2 NOx	C2 NOx
Cleaning		C1 Solvent cleaning C1 Swelling D1 Microscopy	C1Aqueous cleaning D1 Microscopy	

A. Technical studies of paintings. On the development of the painting technique: interaction between artistic intention and material aspects

Technical studies in art history, a flourishing discipline in England and the USA, utilises the material properties of the art object as a source of information on medium use and artistic intentions of the painter. Technical studies in art history aim to explore the physical reality of paintings. It does so by the direct analysis of works of art with technical means, supported by studies of artist manuals and other written sources to provide insight into the history of materials and methods of the use of painting materials. Thus, attempts are made to construct narratives of artistic production and subsequent survival and change.

Observations of technique and condition, obtained with scientific methods are pieced together with information on historic technologies, workshop practices, patrons and provenience. Identifications of component materials in combination with investigations of documentary evidence - the mutual reinforcement of science and scholarship – generates valuable hypotheses of artistic intention. Unique contributions to the field and improvements in the interpretation by art historians result from the application of new methodologies and the performance of fundamental studies in a close collaboration with chemists and physicists. Technical studies of paintings therefore strongly builds on the projects outlined in section B and D.

The research is divided in four areas, according to the objects under study:

A1: Oil painting during the Dutch Golden Age.

A2: Later developments in Oil Painting: The appearance of 19^{th} Century paintings

A3: Early developments of oil paint.

A4: Manuscript illumination and miniatures.

A .1. Oil painting during the Dutch Golden Age

The main research activity is to understand in-depth the paint composition and application techniques during this period, with particular attention to the use of more than one type of binder in the paint, the presence of intermediate layers, and the use of unstable pigments which have since undergone change. This will be accomplished through investigations of individual paintings within this period and by historically accurate reconstructions of paint composites.

Studies of the original making and structural build-up of seventeenth century paintings, the nature of the painter's materials and historic paint manufacturing give insight into original painting techniques and workshop practices. Such a detailed investigation into application methods and materials will contribute to an understanding of workshop practices and stylistic developments during this period. This will make these studies of great art-historical value. There is a strong public interest in the technical aspects, working methods, pigments and colorants that were used by the Dutch masters of the seventeenth century.

With respect to the treatment of paintings, the knowledge of the variety of media used by artists would not only help explain causes of degradation in 16th and 17th century works, but also aid in the choice of cleaning agents and consolidants, which at present is based upon the assumption of the binding medium (see **D1**) being exclusively oleaginous. Infrared reflectography and other surface examination methods (see **D2**) will be used as a lead-in investigation.

Paintings in the Oranjezaal of the Royal Palace Huis ten Bosch, the Rijksmuseum, the Mauritshuis and other Dutch museums will be the prime objects of examination.

A.1.a. Oranjezaal

The Oranjezaal in the Royal Palace Huis ten Bosch holds a large-scale paintings ensemble by famous artists from the Republic and Southern Netherlands, like Jacob Jordaens, Gerard van Honthorst, Salomon de Bray, Caesar van Everdingen, and others. These paintings are extremely well documented, have been subjected to only very few treatments, and are almost in a 'virgin' state. They can be taken to represent the advanced stages of seventeenth century painting techniques. The current restoration project (1998-2002) offers a unique possibility to complement earlier studies (also in the context of MOLART I) on painting technique and interpret the results in a broader context.

This ensemble poses various questions relating to style and technique. All the paintings of the ensemble were made within the rather strict confinements and demands of the architecture. The dimensions of the canvases, the subject matter, the direction of the light, the height of the painted horizon etc. were all prescribed by the architect / manager Jacob van Campen. While such conditions were very similar, the paintings of the ensemble are strikingly different in style. This raises questions about the relationship between style and technique. To what extent are stylistic differences reflected by different techniques or by different choices of materials? In what way is style affected by the origin of the painter? Are the working methods of painters from the Southern Netherlands, i.e. Jordaens, Van Thulden, Coques, and Boschaerts, different from those of their northern colleagues? Did Flemish painters use different materials than painters from the Republic?

These questions are related to a number of observations on technical aspects in the ensemble. Only the reds in two paintings by De Grebber showed signs of discoloration that could very well be so called meta-cinnabar. If this is the case, could this be related to his methods or the origin of his materials? Similar questions also apply to the particular cracking pattern in the painting by Lievens or the possible use of aqueous binding media, specifically for the blue pigments in works by, for instance, Honthorst, Jordaens and Lievens. The occurrence of ultramarine disease in this respect deserves further examination. In portraits on the central piece by Jordaens organic pigment lakes appear to have been used that are conspicuously different from the lakes he used elsewhere in the painting. It is likely that Flemish painters used other lake pigments than their northern colleagues. Such questions demand analyses of pigments, media and organic colorants. Also the exceptional degree of finish in the painting by Lievens may relate to the particular circumstances of the commission. Determination of lead isotope ratios, with TIMS, will lead to good insight in pigment provenience.

The painters who worked on the Oranjezaal ensemble also made smaller paintings for the open market. To what extent are handling of paint, building-up of paint layers, use of materials, and style affected by such differences in dimensions? Such smaller paintings often have had a troubled conservation history, which is contrary to the state of the Oranjezaal paintings. A comparison will provide us with better insights of technical relations between paintings made on commission for a stable environment vs. paintings that were made for the open market.

This project will be concluded in 2003.

Interested institutions: SRAL, Rijksmuseum.

A.1.b. Developments in Painting Technique and Style

The Dutch seventeenth century is of great interest as different techniques and approaches have developed in answer to the demands of the market. Over the century there were continuous technical developments leading to process- and product- innovations. The solutions to these economic demands may vary from almost direct 'alla prima' painting with relatively cheap materials, via very elaborate methods using high quality pigments over 'dead-coloring' systems, to rigid academism.

An important stylistic shift resulting from artistic and economic competition took place in the second and third decades of the seventeenth century. This is most prominent in the work of Esias van de Velde who developed important innovations from his earlier compatriots Gillis van Coninxloo and Roeland Savery. These innovations were taken further, with different emphases, by painters like Jan van Goyen, Knipbergen, Porcellis, and Salomon van Ruysdael. Almost concurrently, by the 1640s Amsterdam had taken over the position of Antwerp as the foremost staple market for pigments, organic dyestuffs and other paint materials. These developments must have affected the choice and qualities of the painters' materials, as well as the way these materials were applied. These developments will be examined in a number of representative paintings from Dutch collections. Materials and working methods of painters like ter Borch, Metsu, de Heem, Netscher and van Mieris will be examined and compared with those of painters like Adriaen Brouwer, Adriaen van Ostade, Govert Flinck, Abraham van Beyeren, van der Neer, or Philips Koninck. Also the technical development of painters whose workshop practices changed considerably towards the use of more complicated layering structures, like Nicolaes Maes, or Gerard Dou, will be examined.

In this context various problems of seventeenth century paint formulation will be addressed. These include the fading of indigo, the photo-oxidation of flavonoid yellow and anthraquinone red glazes on paintings, as well as the discoloration of smalt. Opalescent globular transformation zones originating from lead-bound preparatory layers were observed in paintings by Frans Hals, Rembrandt, Johannes Vermeer, Abraham Bloemaert, and Daniel Seghers. Study of cross-sections with light microscopy, FTIR chemical imaging and perhaps X-ray diffraction, as well as that of "historically-correct" reconstructions will aid in understanding the cause of the phenomenon. Another, still poorly understood, feature of deterioration is the increased transparency of paint layers. This problem, resulting from changes of refractive indices of inorganic pigment material and organic binding medium will be further examined.

Seventeenth-century painting is generally considered 'pure' oil painting. Recently suggestions have been made that also proteinaceous/aqueous media were utilised for specific areas of the painting, for certain layers or for certain pigments. The use of proteinaceous/aqueous media for the imprimatura and, or the undermodelling (doodverf) is not resolved. A study of the binding media of these lower layers will contribute substantially to a more complete understanding of the working process in the artists' studio. This would pertain specifically for painters who worked in a rather 'tight' manner demanding complex paint stratigraphies, as opposed to painters working in more 'loose' manner. This differentiation may probably be marked by variance in quality grades of materials used.

This project requires the application of archival and technical manuscript study, the preparation of historically accurate reconstructions, application of surface examination methods (see **D2**) and analytical microscopy methods (see **D1**).

The results of these studies could be disseminated to the general public in a publication accompanying an exhibition in 2007 / 08.

Interested institutions: Rijksmuseum, AMOLF, Mauritshuis, ICN, RKD.

A.1.c. De Lairesse and Classicist Painting: Materials and Methods

The ‘pictor doctus’ had different approaches, and thus different technical demands than the ‘pictor vulgaris’. Classicist painting, largely driven by art-theoretical considerations, was done with different use of materials. The technical peculiarities of this extremely important art historical development have hardly ever been the subject of investigation. The materials end methods of application will be studied in the works of classicist painter Gerard de Lairesse and other painters of decorative ensembles like Hondecoeter, Glauber, and de Wit. The analytical work will be supported by information from de Lairesses own publication from 1707. From his hand we can examine conventional easel paintings as well as an ensemble from a palace interior (Great Hall of the Royal Palace Soestdijk) This activity therefore ties in quite neatly with the examination of the Oranjezaal paintings

Observations on the paints and their particular characteristics and on the paint layer structures that result from the scientific analyses will be evaluated in relation to paint recipes or painting instructions that derive from contemporary documentary evidence. Recently discovered technical sources, will be studied in relation to the technical examinations, and worked out in critical, annotated text editions. This material, combined with the results of reconstructions and scientific analyses will provide a proper understanding of historically used techniques and their consequences for conservation. Also depictions of painters studios (engravings, sketches, drawings, paintings) may serve as documentary sources of information on seventeenth-century workshop practices.

This project requires the application of archival and technical manuscript study, the preparation of historically accurate reconstructions, application of surface examination methods (see **D2**) and analytical microscopy methods (see **D1**).

Interested institutions: Rijksmuseum, AMOLF, Mauritshuis, ICN, RKD.

A.2. Later developments in Oil Painting: The appearance of 19th Century paintings

The working methods, techniques and materials Dutch painters used have changed drastically during the 19th century. Not only the changes in the manufacture of the paint, from hand grind to machine grind, have influenced the behaviour of the paint in manipulation, appearance and ageing, also the application of new media, dryers and pigments did so. In addition aesthetic theories, colour theory, historical reflections on the techniques of earlier periods and the discovery of new techniques like photography have imposed an increased influence on the change of the applied methods, techniques and materials of painting during this century.

The traditional techniques, ruled and controlled by the structure of the guilds and studio traditions from the 18th century evolved to the application of more individual, independent and non-traditional techniques with a different and ambiguous attitude to durability. This has often resulted in dramatic defects of the paint films that often face conservators with major restoration problems today. Fundamental aspects of some of these phenomena have been studied in the context of MOLART. For example, MOLART is addressing the effect of additives (asphalt, balsam, resin) on the oxidation and cross-linking i.e. the drying properties of oil paint.

Soft and soluble paint layers or varnish layers that belong to the work of art cause difficulties in the cleaning and varnish removal from paintings. In addition, other paint defects such as drying cracking (alligatoring), unintended transparency, darkening, opalescent gelification, blanching and colour changes seriously affect the interpretation of the painter’s intent. The intention of the artists and the appearance of their paintings in relation to these developments are not very well known and understood. This makes it very difficult to develop restoration and conservation strategies or decisions for the paintings from this period. We need more scientific and historical data to construct a historically justified image of the original appearances as a base for our decisions in conservation and restoration of 19th century paintings.

Improved knowledge of paint materials and application techniques from the 18th and 19th century should lead to a greater understanding of the factors that are responsible for these paint defects. In 2000, a pilot research project by MOLART and ICN on "Colour changes in 19th century paintings" was established as a preparatory project for this research resulting in historical evidence on both the intentions of the artists and the application of certain materials and techniques.

A.2.a. The influence of paint composition on the occurrence of paint defects in the 19th Century

As stated above. Paintings from the late 18th century and the 19th century often face conservators with major restoration problems. Soft and soluble paint layers or varnish layers that belong to the work of art often cause difficulties in the cleaning and varnish removal from paintings. In addition, other paint defects such as drying cracking (alligatoring), unintended transparency, darkening, opalescent gelification, blanching and colour changes seriously affect the interpretation of the painter's intent.

The paint defects have often been related with bad drying of the paints due to the use of, for example, bituminous substances and/or excessive use of dryers. Improved knowledge of paint materials and application techniques from the 18th and 19th century will lead to a greater understanding of the factors that are responsible for these paint defects, but also of methods and materials used in *e.g.* the 17th century.

In this project, the influence of painting materials (including manufacturing or preparation) in combination with painting technique is studied. To this end, studies will be made on the contents of 19th century paint on the basis of analytical studies of original paints from tubes and palettes as well as painting studies. These studies will be focused on representatives of Hague School and put in an international context. The original intent of the artists will be studied on the basis of (19th century) documentation and studies on particular paintings.

The research done by the PhD student will be focused on the influence of layer structure in combination with certain pigments, lead dryers and additives on the formation of paint defects. To this end, multi-layered paint reconstructions will be made. This will be done on the basis of the earlier analytical work on painting materials and paintings' studies, in combination with documentary information on paint manufacturing (MOLART, 19th C. project). The reconstructions will be artificially aged and studied using the appropriate analytical chemical and physical methodology. The relevant findings will be fed back to the painting studies.

The paintings research is carried out at ICN (microscopy, analytical chemistry) and in the museums (photography, archival work). Additional (technical) art historical research is carried out at ICN. Links with the Onderzoeksschool Kunstgeschiedenis will be further explored. Links exist with other De Mayerne sub projects D2, B3, B4, C1, D1 (DTMS at AMOLF). The reconstruction research is carried out at ICN. TUE provides the expertise on physical analytical methodology.

Interested institutions: ICN, UvAmsterdam, TUEindhoven, Van Gogh Museum, Rijksmuseum, Museum Boijmans van Beuningen, Kröller-Müller Museum, Tate Gallery London, CCI Ottawa.

A.2.b. Technique and Media of van Gogh

The Foundation Vincent van Gogh Museum is proposing to develop a joint project on the technique of the painter Van Gogh and the behaviour of his painting materials. This project is embedded in art historical studies of the vast archive available on his work by L.Tilborgh and co-workers. Ella Hendriks and co-workers are re-examining all paintings in the restoration workshop of the museum and a catalogue raisoné with technical details is in development.

There is a general interest in the pigments, colorants, binding media and additives that Van Gogh has used to make his paintings. The methodology to determine the chemistry of his paints and their present condition of the pigments and binding media requires advanced imaging microscopic spectroscopic and mass spectrometric methods. The technique of microscopy laser desorption Inductively Coupled Plasma Mass Spectrometry is proposed to determine the trace element signature of van Gogh on the basis of his paintings, tube paints and paints from his palette. The object being to establish new markers for authenticity and to find out how unique his paint composition is in relation to other painters of his time.

The microscopy-imaging methodology applied (see D1) can also help in the clarification of questions concerning photo-oxidation, the condition of proteinaceous intermediate varnishes and the original glossiness of the paint. The stability of a number of van Gogh's paints is very poor. Photobleaching (fading) has seriously affected the original appearance of some of the paintings suggesting that discoloured spots are often faded areas. Analysis of remnants of the photo-oxidised materials could be useful for the reconstruction of the original composition. Egg white varnishes have been used that tend to lose their transparency in the course of time. Imaging SIMS is proposed to establish whether oxidation of the cysteine bridges in the proteins is the cause. The rheology of the high impasto painting method of Van Gogh is of special interest. It is unclear how Van Gogh has manipulated his paint to obtain the desired effects. Whether his media contain additives to make such effects possible will be investigated. HR-SEM will be applied to investigate the phenomenon of the loss of the glossiness of the paints after removal of unwanted varnishes.

This project requires the application of spot analytical methods (see DI) using LM, imaging UV/VIS spectroscopy, imaging FTIR, imaging SEM/EDX and imaging SIMS. Wet chemical methods and mass spectrometry (GCMS, DTMSMS, LDMS) will be performed on selected samples. LD-ICPMS is foreseen in collaboration with Prof. Günter (ETH Zürich) is interested to participate in studies of trace metal composition analysed in cross sections (spot size 5 micron).

Interested institutions: Van Gogh Museum, AMOLF, ICN, ETH Zürich, CCI Ottawa, Carnegie-Mellon University.

A.3. Early developments of oil paint

The main research activity is to study the initial developments in the technique of oil painting.

A.3.a. The ‘secret’ of van Eyck

The paintings by Van Eyck are generally considered to mark the beginning of modern oil painting technique. Although van Eyck is no longer credited for the invention of oil painting, his works show a remarkable improvement of the technique. What constitute these improvements? Many hypotheses have been proposed for the technical innovations that van Eyck may have introduced. Explanations vary from the purported use of combinations of certain types of clear and drying oils, the application of volatile essential oils, the use of certain metal salts as drying agents, the addition of resinous substances, to the use of particular fatty emulsions.

Technical comparisons will be made between paintings by van Eyck and those from the circle around him, and pre-Eyckian paintings like the panels by Broederlam and the early fifteenth century Cologne school.

This project requires the application of archival and technical manuscript study, application of surface examination methods and spot analytical methods. Occasionally wet chemical methods and mass spectrometry will be performed on selected samples.

Interested institutions: Rijksmuseum, RUGroningen, AMOLF.

A.3.b. From tempera to oil paint

This study aims to survey, mainly Italian, paintings from the transition period around 1500, in order to characterise the developments of painting techniques during the intermediate stages between egg tempera painting and oil painting. The introduction of oil painting began around the end of the fifteenth century. During these formative years painters developed different solutions to overcome problems inherent in the new technique with various problems in deterioration resulting. Neither the paint defects nor the technical aspects that lie behind the famous disegno-colorito controversy are sufficiently explored. The results of examinations of the paintings and the analyses of the various materials will be evaluated in light of evidence from published and unpublished contemporary technical written sources.

These were the formative years for the technique of oil painting in Europe. This period marks the beginning of oil painting and thus marks a crucial moment in art history. Without Bellini and Giorgione there would have been no Titian; without Titian, there would have been no Rembrandt. The results of the examinations of the paintings and the analyses of the various materials, should be evaluated in the light of evidence from published and unpublished contemporary technical written sources. During the short period that the transition took place, painters developed different solutions to overcome problems inherent to the new medium. Different methods were developed for the preparation of the oils; various additives to promote the drying of the oils were introduced; new pigments appeared on the palette. All these rapid changes and adaptations resulted in various problems of deterioration. In this context the techniques of some of the worlds most prominent masters like the Bellini, Titian, Giorgione, Moroni, Tintoretto can be studied in their most important works.

This research is facilitated by the presence of a large array of sample material taken in the past (for example the van Asperen de Boer collection of cross-sections). These samples can now be examined systematically using new insights on the behaviour of proteins and fatty acids, and recently developed analytical and imaging methods.

Information of the protein-oil chemistry in the paint will be quite important to interpret the analytical data and to understand the information on the present condition (see project B2). This project requires the application of archival and technical manuscript study, application of surface examination methods (see D 2) and spot analytical methods (see D1).

Interested institutions: Rijksmuseum, RUGroningen, AMOLF, UvAmsterdam, SRAL, ICN, CCI, Rijksmuseum, Kunsthistorisches Museum Vienna, Koninklijk Museum voor Schone Kunsten te Antwerpen. (Collaboration with the National Gallery, London and the soprintendenza ai beni culturali in Venice will be pursued).

A.4. Manuscript illumination and miniatures

The scientific study of miniatures is a fundamental and new area of investigation. Miniatures have quite particular and characteristic problems of conservation. Many of these problems are related to the carbohydrate-based binding medium that was used in some of the colours. In other cases these media are proteinaceous. Deterioration of these media leads to poor cohesion (crumbling, powdery paint) or poor adhesion (paint loss in chips or flakes). Since organic colorants were extremely important in the making of miniatures, fading of those colorants is a recurrent problem. Furthermore, a number of later Dutch artists were known to have been both panel painters and illuminators, such as Petrus Christus, Gerard David, and Simon Bening. To date, very little is known about such inter-related painting activity, either in terms of its extent or its technique.

Recent advances in design of analytical equipment made it possible to develop methodologies of extensive *non-destructive* analyses of painted objects. It is proposed to examine a number of miniatures ad manuscripts with a combination of non-invasive analytical techniques as described in (**D2**)

Aside from the information to be culled from illuminations themselves, a wide range of knowledge about material aspects and working procedures can be gained from technical documents. Contemporary written sources on manuscript illuminations such as recipe books, workshop manuals, treatises of paint manufacturers, apothecary lists, patent issues, workshop inventories and the like contain information about the origin and production of the pigments, the types of binding media, the composition of paints and paint mixtures, and build-up of the paint layers. These factors may affect the ageing properties of the paint. Research of written sources contributes to the formulation of relevant questions in scientific investigation of illuminations and to the proper interpretation of the results of such investigations. It is proposed to include scholarly and scientific work on the mediaeval model book in Cologne (Historisches Archiv Ms W Oct. 293) in this context. However, concerted efforts should also be devoted to the further discovery and disclosure of relevant technical texts. It is proposed to thoroughly study these texts, providing them with English translations and technical and historical comments on the basis of historically valid reconstructions. These studies should be linked with research on paintings within an interdisciplinary approach. Results of scientific research on paint materials in order to identify pigments, colorants and binding media, infrared reflectography etc. should all be taken into account to create a good understanding of the working methods.

The studies proposed do not have to be confined to western cultural heritage only. The Museums voor Volkenkunde in Leiden and Rotterdam have unique Indian and Japanese illuminated manuscripts and prints in their collection which require study as part of a rational conservation plan. It is proposed that the De Mayerne program team will assist the restoration studios of these museums with the identification of the pigments and binding media.

This project requires the application of archival and technical manuscript study, application of surface examination methods like IRR and XRF (see D 2) and spot analytical methods (see D1) using LM, imaging UV/VIS spectroscopy, imaging FTIR, imaging SEM/EDX and imaging SIMS. Occasionally wet chemical methods and mass spectrometry (GCMS, DTMSMS, LDMS) will be performed on selected samples.

Research in many of these sections above will focus on documentary sources, reconstructions and the close examination of actual illuminations. Technical documentary sources must be studied across the centuries in order to provide comprehensive information. The earliest sources are limited in number with technical information that is either fragmentary or lacking in context. In many cases an accurate interpretation can only be made by studying later texts, which provide greater detail on the same subject matter. Since no one text written at any time provides all the information needed, the collection of recipes from many sources allows a more complete understanding of the preparation of artists' materials. Documentary sources providing information on workshop practices will naturally be pursued alongside the technical sources.

Interested institutions: Rijksmuseum, RUGroningen, AMOLF, ULeiden , UUtrecht, RKD, Museum Meermanno-Westreenianum, Koninklijke Bibliotheek, Universiteitsbibliotheken Leiden, Amsterdam, Groningen, Koninklijke Bibliotheek Brugge.

B. Changes in material properties of paints, glazes and varnishes

A greater understanding of the complexity of paintings and painting materials will contribute strongly to our current understanding of the invaluable works of art. Traditional paint formulation methods differ greatly from present day paint formulation. Technical art history will benefit greatly from multidisciplinary studies between historians of painting materials and chemists on the complex details of the chemistry of traditional materials and the methods of paint preparation and use. The traditional natural substances used by artists and craftsmen undergo major changes in chemical composition due to light and metal induced oxidation processes. Oxidation has to take place in order to obtain solid paint films. Beneficial oxidation however changes in destructive oxidation in the course of time leading to degradation processes that conservators wish to stop. The De Mayerne program proposes a number of fundamental studies aimed at improving our understanding of the mechanisms of chemical change taking place in oil paint, proteinaceous media, varnishes and colorants. The relationship between molecular level changes and the resulting changes in physical properties require special attention as micro-cracking, warping and paint loss are a continuous source of concern in the care of museum collections. This knowledge will improve our current understanding of paintings and other museum objects, aid in the reconstruction of the original appearance and suggest improvements in conservation methodology.

B.1. Ionomeric structure of oil paint: co-ordination chemistry in traditional paints

This project will concentrate on theoretical and experimental studies of the co-ordination chemistry in paint layers to explain changes in paint chemistry. On the basis of the results gained by the analytical work that has been done and is being done by MOLART, it is proposed to perform fundamental studies on the behaviour of metals like lead, copper, cobalt, manganese, iron and etc. in their complexing reactions with the constituents of paints. This study is of great relevance for a better understanding of the behaviour of lead white, smalt, azurite, Sienna and omber in ageing oil paint. It will elucidate the specific role of copper in copper glazes and the interaction of binding medium constituents with copper supports. Furthermore, it will improve our understanding of the effects of competing ligands such as terpenoids, acids and certain alkaline cleaning agents used by conservators in the past and even today.

The study will build on the ionomeric oil paint model developed by MOLART but could include polyanionic proteinaceous material as well. The complexes will have to be studied both in non-aqueous and in aqueous media, in order to mimic the processes in the ageing paint as well as the possible reactions during the action of aqueous cleaning agents. The work will focus on, but not necessarily be restricted to, the modelling of the formation of fatty acid and terpenoid acid complexes of lead, copper and cobalt. The action on the compounds of simple co-ordinating groups and anions like fatty and terpenoid acid and hydroxy groups, chloride, sulphate, carbonate and acetate will be studied. The work is to be combined with advanced spatially resolved imaging of samples from paintings using imaging SIMS, LDMS and FTIR at AMOLF.

Special attention will be given to the problems of changes in transparency and lead white diseases with a particular emphasis on lead compounds. Lead is one of the most ubiquitous substances in traditional painting. Lead white, the "light" of the painting, was used alone; in mixtures with many pigments; and in ground preparations. A variety of lead compounds were routinely used to treat the oil prior to painting as well. Very little research has concentrated on the molecular relationship between lead compounds and the oil binder, yet the interaction of these materials is fundamental to the understanding of all aspects of painting, from the stiffness of paint impasto through to the development of cracking.

A better insight into the co-ordination chemistry is also essential for a better understanding of the effects of cleaning in particular aqueous cleaning (see C1a).

Interested institutions: ULeiden, UvAmsterdam, AMOLF, SRAL, ICN, Mauritshuis, CCI Ottawa.

B.2. Proteinaceous networks in media, supports and restoration materials

Proteinaceous materials form an important component in illuminated manuscripts (parchment), tempera and oil paintings. These materials are present as paint binders, in egg tempera, and in underpainting in oil paintings; and are present as intermediate layers within the oil paint composite, for example as canvas sizing-glue, and as glue layers between layers of ground. Proteinaceous materials were also introduced into the paint composite through common restoration treatments, such as glue-paste linings. These materials have not received significant attention in relationship to molecular changes engendered by their preparation methods and subsequent ageing. Proteins undergo many chemical changes dependent on the structure of the constituent amino acids due to elimination, oxidation and condensation reactions. Metal-organic interactions and co-ordination chemical bonds subsequently tie the proteinaceous network together to a solid paint system. Understanding of the properties of these networks and especially the role of metals in their formation and degradation is of vital importance for a better management of the paintings and other art objects where these materials have been used. This information is also of vital importance for the spatially resolved media analysis in cross-sections (see DI) and the use of proteinaceous media in the historical painting production (see A III).

We propose to extend the painting studies with a pilot project to explore the molecular changes in silk, collagen, keratin, elastin, resilin, abductin and their proteinaceous matrix in relation to the methodology of their conservation and to degradation caused by the exposure to the atmosphere (and other environmental conditions). This area is central to questions in ethnography, natural history collections and materials used in modern art installations.

Recent advances in biological mass spectrometry have made it possible to open an analytical window on proteinaceous substances in art that goes beyond amino acid analysis. Strategies based on peptide analysis by mass spectrometry will cast more light on the amino acids in the protein chain that undergo changes due to exposure to oxidising conditions. Various mass spectrometric methods will be used to study the oxidation and cross-linking products of proteins used in art objects.

Interested institutions: AMOLF, UvAmsterdam, UUtrecht, Rijksmuseum, SRAL, Mauritshuis, CCI Ottawa.

B.3. Molecular aspects of traditional methods of paint materials manufacturing

The study of painters' materials is most effectively carried out with a view to understanding not only what ingredients are present, but also the manner in which they were used. This includes the processing of the materials and their application. In preparing for analysis it is also important to be aware of the range of materials that may have been utilised (knowing what to look for) and where they may be found within a paint cross section. Effectively, this applies to all paint materials, because many aspect of the material science of paintings have often been studied in isolation without much attention for the whole paint system nor the methods of usage by painters. Considering the magnitude of this area of study, we propose to focus this approach on the layer structure of oil paintings and particularly on the omnipresent pigment group of lead white.

Since lead white is such an important ingredient in oil paint, a much more complete understanding of its role in the whole paint system is required. Recent MOLART studies of a painting by Rembrandt in collaboration with the Mauritshuis have pointed to chloride impurities in lead white ground layers which appear to have a destructive effect on the stability of the mineral phase of the paint. The mineral phase dissolved and leaves a globular shaped transparent lead soap substance, which becomes a nucleus for new mineral precipitation, but is also a weak spot in the painting. Similar phenomena have now been observed by Wadum and co-workers in a number of other paintings. Lead white as a pigment has been considered as a given with assumed constant properties over the five centuries of historical painting technique. This assumption appears to be challenged now. A thorough historical, chemical and analytical study of this pigment system will be the key topic of the proposal.

Interested institutions: ULeiden, AMOLF, Mauritshuis, CCI Ottawa.

B.4. Modelling the mechanical behaviour of painting materials as a function of climate change and ageing

One of the most important characteristics of paintings and other polychromed works of art which strongly determine their appearance is the formation of cracking patterns. Craquelé can form as a result of a number of processes including (rapid) drying of paint, ageing, restoration, (re) stretching of canvases, movement by changes in climate (temperature and relative humidity). In the worst case, cracking can lead to cupping and loss of paint.

The actual formation of cracks is directly caused by mechanical stresses induced by the above processes. Whether or not cracks form is thus a function of the mechanical and physical properties of the various components of the painting, that is, varnish, paint, ground and support, and the changes of those properties with time. These properties include, among others fracture stress and strain, Young's modulus (stiffness) and the thermal and humidity coefficients of expansion.

In order to 1) determine the cause of craquelé formation in a given work of art, 2) to predict how it will react in the future and 3) to help the conservator in selecting techniques which avoid further cracking, behave in the same manner or do not show crack formation, an understanding of the mechanisms for the changes in mechanical and physical properties of the components, and the micromechanics of crack formation and growth as a function of molecular changes and time is required. The purpose of this task is to determine these micromolecular relationships. The results of this project can then be applied to macroscopic models for the mechanical behaviour of paintings, which use finite element analysis. For example, a complementary programme for this type of modelling has been proposed to the STW. In that programme, micromechanical properties are required to define the (micro)elements for the finite element models and to understand the macroscopic behaviour of simulations.

The work in this project will be conducted on selected materials used for the classes of paintings which are to be investigated in Part A of the overall Mayerne programme and consists of the following tasks:

1) In order to properly select representative materials for this study, information is required on the location, form and distribution of craquelé as a function of types of paints, ground and supports (canvas, wood or metal), relative position of different types of paints, construction and dimensions of the work of art, thickness and number of layers ,etc. Both visual observation and the use of a high resolution CCD-camera (see D2) are required for this task. This work builds on initial research conducted on craquelé in MOLART I
2) The mechanical properties of the selected components will be determined, first individually and then in combination. Tensile tests will be conducted to determine the previously mentioned tensile properties as a function of ageing time (changes in molecular structure) and variations in component structure, e.g. volume fraction of pigment, type, geometry and distribution of pigment, local properties of the (aged) polymer matrix. The fracture (cracking) mechanism(s) of the materials will be determined using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) in combination with EDS. For macroscopic properties, tensile testing equipment similar to that used by Mecklenburg must be built. For studies of the micromechanisms of cracking, an *in situ* fracture stage will be built for a light microscope and for the SEM.

3) The physical properties, coefficients of expansion (temperature and humidity) of the selected materials will be determined as a function of their condition. In order to calculate the stresses as a response to climatic changes (temperature and humidity) coefficients of expansion must be determined. These will be determined as a function of ageing time (changes in molecular structure). Using the results and the stiffnesses measured in iii, the stresses in works of art can be calculated. Where possible, samples from the paintings will also be tested. In those cases, it will not be possible to directly measure

stress levels, primarily because of the size of the samples. This work will thus require dilatometry measurements in a high-resolution optical microscope with climate stage.

4) Cupping and the ultimate loss of paint or protective coatings is a function of the interfacial strength between paint or coating layers with each other and with the support. There are a number of “standard” methods for measuring adhesive strength, but it is likely that a method for these thin layers must be developed for this task. In addition, chemical/surface analysis of the interfaces will be performed, e.g. Auger, XPS, FTIR, Raman ellipsometry, etc. The relationship between adhesive strength and molecular/chemical structure of the interfaces will then be determined and modelled to predict deformation and paint loss and evaluate restoration procedures on the mechanical properties of the paint film.

5) The results of 1-4 will be used to model the behaviour of the various materials as a function of climate changes and ageing and will be immediately applied to more applied modelling being conducted in an STW programme proposed by ICN and the three technical universities.

Interested institutions**:** ICN, TUEindhoven, UTwente, Rijksmuseum, SRAL, Royal Academy of London. This project will require additional investments.

C. Effects of restoration procedures

The study of cleaning methods is of singular importance not only for understanding how solvents interact with paint for contemporary restoration treatments that allow safer methods of cleaning, but also in relation to understanding changes in paintings caused by cleaning methods used in the past. Phenomena which influence our current interpretations of images, such as blanching, colour changes, and surface disruptions thought to have resulted from harsh overcleaning in the past, will be better explained as a result of this work. The effect of solvent cleaning has been a topic of one PhD study within MOLART. Fundamental studies on the chemical changes in oil paint and varnish (two other PhD theses) have aided in the understanding of the ageing processes that take place. Despite the continued interest of restorers in the solvent sensitivity of paintings, it is proposed to devote special attention to the effects of aqueous cleaning media on mature ionomeric oil paints. Such studies require more fundamental knowledge of the co-ordination chemistry of such paints and the possible disturbance in co-ordination that cleaning agents may cause. Additionally, the effect of moisture itself as an agent affecting the stability of the ester bonds in young oil paints and the co-ordination chemistry in mature paints will be an important topic in these studies.

A second topic of considerable interest emerging from MOLART is the selectivity in removal of fractions from aged varnish, as a consequence of “cleaning” with organic solvents. Partial cleaning is a well-accepted method in certain countries but questions remain whether varnish can be removed partially without leaching the desired remaining layers.

C.1.a. Effects of aqueous cleaning methods on mature oil paint systems

Oils must cross-link and oxidise to form an oil derived polyester network that upon ageing results in a negatively charged network (an ionomer), which is bound by positively charged metal ions from the pigments or dryers. Proteins in egg tempera paint also undergo chemical changes leading to a negatively charged protein network due to elimination, oxidation and condensation reactions. Metal-organic co-ordinating bonds subsequently tie the proteinaceous network together. Models of both systems were developed by MOLART as working hypotheses to describe the fate of natural materials such as oils and proteins in transition metal rich paint environment. Understanding of the properties of these networks and especially the role of metals in their formation and degradation is of vital importance for a better management of the paintings and other art objects where these materials have been used.

Water based restoration methods, such as cleaning gel methods of Wolbers, cleaning methods using ammonia, citrate etc. but also paste lining techniques, could strongly influence the binding capacity of mature hardened paints. Sometimes over-paints in oil can only be removed by alkaline agents. However, more and more chelating agents are used, such as triammonium citrate, to remove surface dirt and grime (wall paintings, sculptures, paintings). Apart from leaching and swelling effects caused by the large amounts of water used, these sequestering compounds theoretically can endanger the paint layer (the ‘polyanionic’ paint network) by breaking bonds between metals (pigments) and the oil network. These effects are proposed to affect the mobility of the fatty acids in the paint also. Special attention will be given to the effect that water or moisture has on the long-term stability of the paint, especially how it affects the solvent extractibility later on. Cleaning using aqueous cleaning agents is therefore worthwhile examining thoroughly in a multidisciplinary project.

This project interacts strongly with B1 that focuses on the fundamental co-ordination chemical aspects of metal co-ordinated oil paint systems. It is proposed to investigate the effects of historical and present day restoration methods on the chemical stability of the paint.

Interested institutions: SRAL, ULeiden, AMOLF, Museum Van Gogh, ICN, Mauritshuis, CCI Ottawa.

C.1.b. Partial cleaning of varnish

Partial cleaning or thinning of a varnish is meant to reduce the interference of the yellowed varnish with the perception of the colours of the painting by removing part of the aged varnish using solvents. This type of cleaning is controversial. The varnish as part of the artist's intent and the role of discoloured varnish as an aesthetic effect are important subjects of debate by curators and conservators. Little is known about the effects of partial cleaning on the molecular level. It is clear that oxidised terpenoids are readily soluble in solvents and leaching of the residual varnish remaining on the painting surface can not be ruled out. Earlier studies by MOLART led to the hypothesis that partial cleaning results in an increase in higher molecular weight fractions on the surface of the painting. The proposed research will test this hypothesis and focuses on the solubility of oxidised and cross-linked fractions in aged varnishes, and the characterisation of the layer of aged varnish that is left behind on the paint surface using spectroscopic and mass spectrometric methodology. A second aspect of partial cleaning is the hypothesis that the paint layers are not affected by this cleaning approach and that the residual varnish actually protects the outer layers of the paint. The proposed research will challenge this idea by comparative studies of the surface by HR-SEM and determination of the organic chemical composition of the varnish, the paint layers and the underlying support using "wet" chemical techniques, microscopy-spectroscopic and microscopy-mass spectrometric approaches. Relative concentrations of fatty acids in cross sections with a I micron resolution using negative ion SIMS before and after cleaning attempts will be determined to find out whether fatty acids are being transported through the paint layers as a consequence of solvent exposure. Studies are proposed on paintings, lined paintings and suitable model systems. The proposed work builds on pilot studies by MOLART (Van der Doelen) taking place in the context of the Oranjezaal restoration project.

Interested institutions: SRAL, AMOLF, ICN, ETH Zürich.

C.1.c. Swelling of artists' paints in organic solvents and aqueous solutions

Most old, non-original varnishes found on paintings are of the spirit varnish type, based on low-molecular weight tree resins (dammar, mastic, etc.). Such materials are unstable and photo-oxidise rapidly. In addition to yellowing, on ageing they become chemically more polar, more acidic and, to some degree, more polymeric. It is perfectly logical that organic solvents and mildly alkaline solutions are the primary chemical tools conservators look to in attempting to remove such coatings. This process is not, however, without certain risks to the original paint.

For organic solvents, two principal sources of risk have been identified: *swelling* of the binding medium, and extraction of soluble organic components (*leaching)*. In comparison, the swelling response of paints to solvents and other cleaning agents is remarkably under-studied. It could be argued that swelling presents a more significant, acute element of risk in the cleaning of paintings. In the swollen condition, pigment binding is reduced and pigment is vulnerable to removal by the mechanical action of, say, a swab applied to the surface. Limiting the degree of swelling of the original paint is, therefore, one of the key means by which the conservator seeks to exert control over the cleaning process. Within the field of conservation, the pioneering work of Stolow, now more than 40 years old, is the only study on artists' oil paints; and within the wider field of paint technology there is but a small handful of publications on swelling of paints by solvents and aqueous liquids. Crucially, the degree of equilibrium swelling has been identified as an indicator of the magnitude of solvation interaction between a liquid and the organic phase of the paint. Solvents vary significantly in their swelling power according to polarity, chemical functionality and molecular size.

Recent perspectives on the chemistry of the ageing of drying oil paints also suggest an increasingly polar character to paints with increasing age, as well as a significant diminution of organic binder phase through diffusion and/or volatilisation of mobile components and scission products. Both oxidation and hydrolysis will lead to the formation of polar oxygenated functional groups in the organic binder phase of aged paints. It has been postulated by Boon *et al* that hydrolysis may indeed be a significant alteration pathway for certain drying oil paints. In the Boon model the original polyester glyceride network of the cured paint film is converted by hydrolysis to at least a partial polyanionic network. It is suggested that metal ion/carboxylate co-ordination may contribute significantly to paint film cohesion. Given the appreciable loss of organic binder phase in old paints, such co-ordination cross-links may be important in holding the paint film together. This model also suggests an increasing sensitivity with age of paint films to polar, aqueous environments. Furthermore, paint film cohesion could conceivably be disrupted by processes other than the simple solvation-swelling of the cross-linked triglyceride network, meaning that physical swelling - in the sense of actual dimension change - may be quite small, if at all measurable. Taken in parallel with possible negative dimension changes due to leaching, attempting to distinguish the relative solvency powers of various liquids by means of the dimension change caused to paint films may not actually be viable for significantly aged paints. Alternative approaches to monitoring paint/solvent interaction may be more fruitful; for example, measuring the softening of the paint, or other change in mechanical properties, caused by solvent sorption.

The nature of pigment in the paint influences the pattern of drying and deterioration. Pigmentation therefore has considerable effect on solvent-swelling response, as do the proportion, nature and condition of the organic binder. Oil paints also become more acidic on ageing, and it seems likely that acid/base interactions will have an increased influence on swelling behaviour of old paint. Swelling of young linseed oil paints has been shown to be quite strongly dependent on pH. It is an intention of the project, therefore, also to examine the swelling of paint films caused by alkaline solutions which, like organic solvents, are commonly used in the cleaning of pictures.

The proposed project seeks to explore relationships between paint film composition, specific solvent characteristics and swelling response. The purpose of the project is to provide scientific evidence that will improve the ‘precision’ with which conservators can deploy these chemical tools in execution of the craft of cleaning paintings. The results are expected to contribute to better understanding of paint-solvent interactions and should form the basis of improved theoretical frameworks for assessing risk and selecting solvents and reagents for the cleaning of paintings. The results will be interpreted in the context of current systems for specifying solubility behaviour (i.e. solubility parameters).

Interested institutions: ICN, SRAL, AMOLF, CCI Ottawa.

C.2. Passive conservation – the effects of NOx and anoxia

Dosimetric studies of the museum environment have pointed out that NOx is a strong oxidising agent that is still very active at very low light levels. NOx is also an acidifying agent that is thought to severely change the paint chemistry making paintings more vulnerable to cleaning with solvents. This project is primarily concerned with a study of the effects of NOx on traditional paint media and paintings. It should seek solutions to prevent or minimise the damage. One option is the development of protective boxes that protects the art from the ambient atmosphere. It is proposed to investigate the effects of keeping paintings in inert atmospheres for prolonged periods of time.

Interested institutions: UvAmsterdam, Museum Van Gogh, AMOLF, Rijksmuseum, Mauritshuis, Tate Gallery.
Note that this project is of interest to CCI Ottawa and some aspects (box design) have been explored at the Getty Conservation Institute.

D. Method development, new instrumentation and data management

Advanced spectroscopic studies of paintings and paintings cross sections give an insight into the construction of the art work, the painting technique and the present condition. The vast majority of the analytical techniques applied to paintings are *destructive*, since for analysis a (tiny) sample from the object has to be taken. In many cases the integrity of the object prohibits any sampling. This disadvantage can be overcome by taking advantage of recent developments in spectroscopy, detector manufacturing and data handling which allow non-destructive imaging of the painting surface, elemental mapping by X-ray fluorescence techniques, recording of ultraviolet, visible and infrared spectroscopic properties of the paint and imaging of the underdrawing using InfraRed Reflectography. A laboratory equipped with this instrumentation, the necessary computer controlled object manipulators and data processing capabilities does not exist in the Netherlands. New types of highly sensitive CCD cameras for the optical, infrared and X-ray range, microfocus x-ray sources, InGaAs PIN photodiodes, allow the construction of ultra high resolution instrumentation necessary to image paintings in the highest possible detail. The data streams from such instrumentation require considerable efforts in data handling, processing and visualisation. These developments make it possible to develop methodologies of extensive *non-destructive* analyses of painted objects.

The microscopic characteristics of pigments and paint layer structure in paintings by different painters reflect idiosyncrasies in characteristic materials, particle size distribution, and paint layer structure that provide useful clues for a better understanding of historical painting techniques. MOLART has contributed to this area of research by development of imaging microscopy, ultraviolet, visible light spectroscopy, imaging Fourier transform infrared spectroscopy and spot selective laser desorption mass spectrometry for analysis of organic compounds in the cross section. Further instrumental development will make it possible to extract much more information from cross sections in order to achieve the challenging perspective of spot selective determination of the composition of the binding medium, imaging of metal-organic complexes using high resolution mass spectroscopy and spot selective determination of the spectroscopic properties of organic colorants and aged varnishes. Studies by MOLART at AMOLF have shown that such detailed studies can be performed on the basis of the existing global archive of cross sections, thus minimising the need to take new samples.

D.1.a. Advanced media analysis of cross sections from paintings by imaging microscopy-spectroscopy and microscopy-mass spectrometry

Paintings' cross sections describe the third dimension of paintings. The superposition of layers, the layer thickness, the grain size, the kind of pigments and the binding medium are important microscopic properties which mark the painting technique of the painter. The distribution of these characteristics is often so unique that it can be used to authenticate paintings or to place a painting in an historical context. The microscopic-spectroscopic and microscopic-mass spectrometric examination of cross sections is therefore of vital importance for technical studies in art history, studies of processes chemical change in paintings and effects of conservation methods.

Imaging UV-VIS microscopy will be used to map the spectral distribution of ultraviolet fluorescence and visible light in order to identify materials in reflected and transmitted light. Imaging FTIR microscopy will be used for chemical microscopy of the materials in cross section. Scanning microscopy LDMS will be applied to study the organic composition of the binding media (oxidation state of the oil and analysis of peptides), resins and organic pigments. Imaging SIMS will be applied to determine the distribution of elemental composition and molecular distributions to study metal organic interactions in samples from paintings. HR SEM-EDX microscopy will be applied to study elemental composition with a resolution of a few nanometer. All this instrumentation is available at AMOLF and can be utilised to develop methodology to study paintings.

XRD studies to examine spots of about 10 micron inside cross sections is presently not available in the Netherlands but is accessible through collaboration with the CCI in Canada. Imaging XPS and imaging Auger spectroscopy when required will be available through collaborations with third parties. Apart from these microscopic analytical techniques, methodology is available at AMOLF to perform supporting mass spectrometric studies of oxidised and cross-linked lipids, resins and proteins.

The proposed research emphasises the use of imaging microscopic spectroscopic techniques to chart the present distribution of mineral phases, organic media and elements in cross sections with the object to improve our understanding of the paint chemistry in a historical context. This project will also involve further refinement of the microscopic techniques. There is a close collaboration with the project A.1 on processes of chemical change in paintings, the project on the media by Van Gogh (A2), and the project on the co-ordination chemistry of oil paint (B1).

This research is strongly interactive with the proposed research in section A1-4, B1, B2, B3 and C1. Data will be compared, processed and disseminated using specially developed software for high resolution image data with the support of the virtual laboratory of Prof. Hertzberger at the UvA. A project leader (postdoc) supported by the De Mayerne Program will direct the microscopic research on paintings at AMOLF.

Interested institutions: AMOLF, Rijksmuseum, UvAmsterdam, Mauritshuis, ICN, CCI Ottawa, ETH, Zürich. AMOLF will support this effort with technical staff and infrastructure.

D1.b. Advanced mass spectrometric research of painting materials.

The molecular structure of paintings materials i.e. varnish, oil paint, tempera paint, glazes, resins and balsam and their ageing products requires high resolution high sensitivity chromatographic separation techniques, advanced mass spectrometric instrumentation and know-how. Techniques and methodologies using various MS techniques developed for painting studies in the context of MOLART are available at AMOLF for research within the De Mayerne program. Instrument time and required methodology can be requested in the context of the project clusters. The new project leader (see D1a) will co-ordinate the mass spectrometric research requested by team members of the De Mayerne program.
Available chromatographic instrumentation consists of capillary GC, HPLC, TLC and SEC instruments and mass spectrometers using chromatographic inlets (GCMS, Py-GCMS, LCMS with FAB, ESI, APCI or thermospray ionisation, TLC-MS). Direct probe MS instrumentation is performed on a 4-sector MS, ITMS, TOFMS or FTMS using Direct temperature resolved MS (DTMS), Laser desorption (LD) MS, Matrix assisted laser desorption ionisation MS and ESI-MS for studies of characteristic ions at ultra high resolution and/or by high or low energy MSMS. Studies of highly oxidised lipids and oils, resin oligo- and polymers, proteinaceous materials and proteins, cross-linked oils, synthetic resins and polymers are among the fractions that may be submitted for study. One fte of technical assistance, the instrumentation and infrastructure will be supported by the Program of Macromolecular Mass Spectrometry at AMOLF.

D.2. Non destructive infrared reflectography of paintings and illuminated manuscripts

The information obtained will be complemented with insights obtained from similarly non-destructive light spectroscopy, performed in various wavelength ranges (ultraviolet, visible, and infra-red). The combined methodologies will lead to an accurate estimate of the variation in wavelengths required for the non-invasive study of manuscript illuminations and miniatures. The information obtained from these combined non-destructive studies is not only relevant for technical studies in art history of paintings (**A 1-4**) but will aid in the study of bleaching and darkening processes in paintings, provide information of the decomposition of certain pigments, the causes of blanching on the paint surface, or the presence of certain siccative additives to the paint formulation, and will provide more understanding of the photoluminescence of varnishes in relation to ageing processes on painting. The same approach will be valuable for a study of the changes in transparency and refractive index. The combined XRF, X-radiography and IRR systems will be mounted on the same X/Y stage, equipped with computer-controlled stepper motors.

D.2.a. Infrared reflectography*.*

Infrared instrumentation (the AIM PtSi IR focal plane camera, “classic” IRR, and other digital IR focal plane arrays) will function in the De Mayerne Program as a component of the core facility, here understood as a combination of equipment and expertise. The employment of such instrumentation is advisable because of its known capability to provide critical information about the larger painting process, artistic production, and artistic intention; it therefore enlarges the possibilities for the integration of various types of material data. MOLART was the developmental phase of the AIM PtSi 640 x 486 IR focal plane camera, and phase of implementation and evaluation is now required. The use of this camera (also in combination with others) as a lead-in technique in the projects (as mentioned above under A.1) will facilitate this evaluation and contribute information about workshop practice, undermodeling or underpainting techniques, as well as the provisional identification of pigments. Some possible applications follow, each of which provides a platform for evaluative study.

A.1.a. Oranjezaal. This complex offers an ideal opportunity to analyze the capabilities of the PtSi camera, for many paintings have already been studied by different IR and IRR devices. In the central piece by Jacob Jordaens, there may be more underdrawing and other lay-in methods to discover than in all other seventeenth-century paintings studied to date. This in itself speaks to the exceptional nature of this painting, both in terms of technique and condition, and makes further study a promising endeavor.

A.3.a. The “secret” of Jan van Eyck. By combining the results of analytical study with existing or new IRR material, the research can be developed to a more fully integrated consideration of the materials and medium of the underdrawing, the position of the underdrawing relative to the isolation layer, and the medium of the isolation layer as compared with other components of the paint-layer structure. Jan van Eyck’s “secret” constitutes a seminal issue in the field of technical studies, but the question is now at an impasse since previous research has produced conflicting results. Revisiting this issue with an array of new analytical methods will result in a major contribution to the historiography of technical studies. Some results may also relate to the conservation histories of the paintings.

A.4. Manuscript illumination and miniatures. This research is ideally suited for a comparative study of infrared instrumentation. A plausible outcome is an accurate estimate of the variation in wavelengths required for the non-invasive study of manuscripts, and, by extension, the frequency with which different filters or even different cameras might be needed in the study of this, and related art forms.

The last application, A.4, is in part of feasibility study, although the evaluation of the infrared instrumentation and an exploratory study of manuscripts can proceed immediately. For extended research, certain devices must be developed that will facilitate the scanning of objects positioned horizontally and produce small motion increments as controlled by computer-driven tripod systems.

Interested institutions: RUGroningen.

D.2.b. UV-VIS spectroscopy

One of the most important parameters for developing preservation and restoration strategies for paintings is the constructed image of the original appearance of the object and the cultural validation of these images in relation to aged appearance. However some aspects of the optical appearance like gloss, transparency, saturation, surface roughness and brush strokes are still not well defined nor do we have the disposal of rational data on these aspects in paintings. The same goes for certain ageing phenomena such as discoloration, darkening, cracking, cupping and crater formation which are recognised as diagnostic parameters by conservators but never rationalised. The reconstruction of the original appearance of the painting will always stay subjective but can be optimised considerably by the development of means, protocols and interdisciplinary research.

Imaging the optical appearance and relating them to the diagnostic knowledge of conservators and the results of art historical and scientific research is therefore a potential fundamental area of research for development of better conservation and restoration procedures.

Objective colour-registration is a first condition for the accurate evaluation of these effects of change, like darkening, discoloration, change in transparency, surface, cracking and cupping, on the appearance of the painting. The processes of traditional photographic techniques used for registration till now have been too vulnerable to detect these changes with a reliable scientific protocol. The registration with high-resolution digital cameras under strict conditions does give the possibility to monitor these changes over longer periods and after different conditions like during transport and climate changes.

Accurate detection of these effects by high resolution (spatial and colour) camera will be employed for monitoring and for the evaluation of the impact of these changes on the appearance of the painting, for colour analysis/discoloration and for the evaluation of restoration procedures like original surface and changes of matteness and saturation during and after cleaning, partial cleaning etc. and dimensional changes/deformations.

This work will include further development of imaging techniques and image analyses, protocols (calibration) based on previous results from EC projects like VASARI and MARC, research at the National Gallery London, Doerner Insitute Munich, and MOLART I (Sybille Schmidt) and by van den Herik et.al. University Maastricht.

Interested institutions: ICN, Centrum voor Wiskunde en Informatica (CWI)

D.2.c. Energy dispersive x-ray fluorescence spectrometry

Energy dispersive x-ray fluorescence spectrometry (XRF) will be used for the qualitative and semi-quantitative identification of elements, mapping out the elemental distribution from pigments over the entire painting.

Interested institutions: Rijksmuseum.

D.2.d. X-radiography
It is desirable to develop a portable scanning X-ray imaging system for the making of X-radiographs, using a small x-ray tube and high-resolution image plates. This will make it possible to utilise X-radiographic methodology on-site in the museum.
Interested institutions: UvAmsterdam.

The instrumentation project in D2 will require investments in:
X-ray fluorescence spectrometer
InGaAs camera, HR color camera + hardware (ICN)
Frame/tripod device for tilt-down positioning of IRR and HR color imaging.
Portable scanning X-ray imaging system for the making of X-radiographs
The program cannot provide these.

Annex 2

Program management

Steering Committee

Establishment
The Steering Committee of the program will, at the start, be formed by representatives of the participating NWO-councils. NWO will establish the Steering Committee for the term of the program and will provide the secretariat. The chairman of the Program Committee will receive an invitation to attend the meetings of the Steering Committee. The Steering Committee will determine its own procedures.

Tasks
The Steering Committee has the following tasks:
1. To decide on the granting of projects based on the order of priority given by the Program committee
2. To evaluate and determine the annual budget of the program
3. To take care of the interim and final evaluations of the program
4. To evaluate and approve reports and project evaluations

The Steering Committee has the right of returning proposals to the Program Committee. It is not privileged to modify proposals by the Program Committee. If it wishes to alter any proposal of the Program Committee, this should be discussed with the committee. Thus, the Steering Committee supervises the broad outlines of the program and should refrain from control regarding the contents of the program. Adjustments in priorities can be made after a first evaluation by Program Committee and Steering Committee.

Program Committee

Establishment
NWO will establish a Program Committee for the term of the program. NWO will provide the secretariat of the committee. The Program Committee is responsible for the program and for the scientific co-ordination of the program.

Tasks
The program committee has the following tasks:
1. To supervise the execution, unity and consistency of the program, according to the approved program proposal. To this end, the committee presents an annual plan to the Steering Committee, together with a budget proposal, including cash planning and a budget estimate for the next years. This proposal fits within the financial framework.
2. To submit a call for proposals
3. To initiate research proposals that can contribute to the objectives of the program
4. To have project proposals judged on quality and relevance with respect to the objectives of the program
5. To formulate an order of priority of the proposals for the Steering Committee
6. To report annually to the Steering Committee on the progress of the research, as well on the budget spending
7. To obtain additional funding for the program from other sources
8. To stimulate collaboration between universities, between universities and users, and between universities and other research institutions
9. To encourage the anchoring of research stimulated by the program in university and institutional research groups
10. To encourage the co-ordination and fine-tuning with other programs and initiatives in the field of research
11. To stimulate the international tuning of activities and the establishment of an international research program
12. To stimulate knowledge transfer

13. To indicate the possible consequences on policy of the research results

Some of the responsibilities of the Program Committee, i.e. the organisation of the meetings within the program and the final editing of the progress reports are delegated to a co-ordinating core group, which will be appointed by the Program Committee from the principal investigators.

Annex 3

Competition: judgement criteria

Applications up to a maximum of 1.0 million guilders can be submitted based on the clusters as defined in Chapter 2. Applicants must form a multidisciplinary research team. The proposals will be evaluated by an international refereeing process and prioritised by the Program Committee.

For the selection of the proposals the following criteria can be applied, with the general condition that the applications fit well into the program.

1. ***Policy aspects***
- fitting into the program
- importance of objects to be studied
- spreading over the themes of the program
- added value with respect to other parts of the program
- collaboration beyond disciplines
- support of other institutions

2. ***Relevance, in particular in art-historical practice***
- cultural/societal relevance
- relevance to the objectives of the program, also on the long term
- knowledge transfer
- coherence; new insights
- technical applicability; prospects on utility of results etc.
- “products” to be supplied

3. ***Scientific quality***

a. ***What is studied?***
- scientific importance
- originality/innovative character of objectives
- clarity of the formulation of a problem; operational feasibility in sub-questions

b. ***How is it studied?***
- adequate approach/ methodology for the objectives set
- originality/innovative character of the proposed approach/methodology
- feasibility
- accessibility of the materials
- clarity of the formulation of a problem; operational feasibility in sub-questions
- is the requested equipment adequate to perform the proposed research
- are the requested finances in good proportion to the proposed research
- work plan etc.

c. ***Who performs the research?***
- earlier results of the researcher, supervising/research group
- earlier results in relation to the proposal
- adequate composition of supervising/research group
- adequate collaboration with others
- feasibility in terms of experience, supervision and logistic facilities etc.

Annex 4

Facilities: abbreviations and availability

DSC	differential scanning calorimetry	
DTMS	direct temperature resolved mass spectrometry	AMOLF
DTMSMS	direct temperature resolved tandem mass spectrometry	AMOLF
ESI-FTMS	electro spray ionisation FTMS	AMOLF
FTIR	Fourier transform infrared spectrometry	ICN; AMOLF
FTMS	Fourier transform mass spectrometry	AMOLF
GCMS	gas chromatography mass spectrometry	ICN, AMOLF
HPLC	high performance liquid chromatography	ICN, AMOLF
imaging SIMS	imaging secondary ion mass spectrometry	AMOLF
IRR	infra red reflectography	Museums, RKD
LDMS	laser desorption mass spectrometry	AMOLF
MALDI/TOFMS	matrix assisted laser desorption Ionisation / time-of-flight mass spectrometry	AMOLF
MC	microchemical tests	Rijksmuseum, Mauritshuis, ICN
PLM	polarised light microscopy	Museums, ICN, SRAL
SEM/EDX	scanning electron microscopy energy dispersive X-ray spectrometry	ICN
SIMS	secondary ion mass spectrometry	
TLC	thin layer chromatography	Rijksmuseum, ICN
XRD	X-ray diffraction	ICN, UvA
XRF	X-ray fluorescence spectrometry	ICN

Abbreviations

AMOLF	FOM-Instituut voor Attom- en Molecuulfysica, Amsterdam
CC	Canadian Conservation Institute, Ottawa
ETH	Eidgenösssiche Technische Hochschule, Zürich
GCI	Getty Conservation Institute, Washington
ICN	Instituut Collectie Nederland, Amsterdam
RKD	Rijksbureau voor Kunsthistorische Documentatie, Den Haag
SRAL	Stichting Restauratie Atelier Limburg, Maastricht