Gilt Leather Artefacts

White Paper on Material Characterization and Improved Conservation Strategies within NICAS

Due to its sensitivity, the conservation and upkeep of gilt leather is often underestimated. It can sincerely be considered as endangered cultural heritage. This publication describes the current state of knowledge from the perspectives of Technical Art History, Material Dynamics, Conservation and Diagnostics, and sets out research directions for 2017-2025.

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FOREWORD

In 2014 with the launch of the Netherlands Institute for Conservation, Arts and Science (NICAS), I took a step into the unknown and discovered the world of Gilt Leather, its historical roots and its importance in the culture of the Northern and Southern Netherlands. These regions were an important production centre of Gilt Leather in the seventeenth century and today the Netherlands and the Flemish region of Belgium are important players in the conservation of Gilt Leather internationally. I discovered that 'gilt' in this case refers to silver overpainted with yellow or orange-brown oil-resin varnish, an economical choice for these objects and one that does not detract from their beauty. I also discovered that these Gilt Leather artefacts have a special character and uniqueness and are at risk, with many not surviving to the present day, for various reasons, including a lack of scientific knowledge to guide the conservation process.

My background is as a scientist interested in non-destructive analysis of objects and materials across different disciplines. Since 2005 I have worked on several conservation projects, including the EU Multiencode and Syddarta projects investigating canvas and panel paintings. In parallel to this project, I am a partner in the NWO Science4Arts project Climate4Wood, investigating decorated wooden objects, and in the NWO NICAS Drawing out Rembrandt project, investigating iron gall ink and paper degradation. Together with my colleagues from RCE, SRAL, RNA, TUD and UVA, we have received seed funding from NICAS to explore the challenges of Gilt Leather across the domains of NICAS, which are Technical Art History, Material Dynamics, Conservation and Diagnostics. The opportunity to host the international workshop on Gilt Leather in Maastricht in March/April 2016 not only reconnected me to colleagues in heritage conservation, but also introduced me to the international experts in Gilt Leather and the challenges they face in the conservation of these complex objects.

I see many opportunities for scientists and conservators to collaborate on the topic of Gilt Leather, a lot of challenges and many unknowns. This is the nature of research, however we would like to make a real difference to future conservation of Gilt Leather objects and preserve them for future generations to enjoy and learn from.

This white paper outlines the state of the art for Gilt Leather within the NICAS framework and I would welcome your feedback, discussion and comments and I look forward to a future collaboration.

Finally I would like to thank Martine Posthuma de Boer for taking the lead in writing the white paper, Eloy Koldeweij for his co-editing and extensive contributions on the art history topic, and my project colleagues, René Hoppenbrouwers, Arjan Mol, Elizabet Nijhoff Asser, Vassilis Papadakis and Bianca van Velzen for their contributions.

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SUMMARY

Among the various types of wall decorations used in the Western world during the 16th to 18th centuries, gilt leather belonged to the most fashionable and costly ones. Despite its appearance, it is not real gold that creates the golden shine, but typically a silver leaf which is coated with an orange-brown lacquer to obtain the characteristic golden lustre. Due to its fragile character, only a fraction of the gilt leathers have survived in situ or in museum collections. Even though some of these gilt leathers are hanging in prominent locations, it is both nationally and internationally an overlooked part of our cultural heritage. Conservation work on gilt leather is a real challenge due to the complex nature of the material, historical craft-led conservation practices and the lack of systematic analytical research of degradation processes.

This white paper presents an overview of the current state of the art in gilt leather research and conservation, and identifies future research directions. It is the result of a cross-disciplinary collaborative research project on gilt leather started in 2015. As part of this an international group of experts in gilt leather met at a Symposium in Maastricht, The Netherlands (March 2016). One of the outcomes of this meeting, covering the topics of art history, conservation, material dynamics and diagnostics, was a research agenda for gilt leather 2017-2025. The results for the different NICAS themes are presented below.

TECHNICAL ART HISTORY

This study has confirmed that there is a need for more in-depth archival research on gilt leather and gilt leather workshops, including the study of inventories, contracts, guild regulations and manuscripts, in the most important production centres of gilt leather in Europe, such as Amsterdam, Brussels, Cordoba, Florence, Mechelen, Paris, Rome, Seville and Venice. Current research into the production technology of gilt leather should be continued, by studying literary sources, combined with reconstructions and material characterization of gilt leather objects and wall hangings. The *Mechelse Secreetboek* is an important, yet undisclosed 17th and 18th century source of paint recipes, which could yield new knowledge on the use of colorants and binding media for gold varnishes, glazes and paints for gilt leather manufacture.

Recently important steps have been made in developing an analytical methodology for integrated material characterization of both organic and inorganic substances of gilt leather, which should be built on and expanded, for example with analytical methodologies to characterize the type of leather (animal breed), the tanning materials, the protein adhesives used to adhere the silver leaf, the coating materials on top of the silver and the 'colouring' ingredients of gold varnishes. The development of a user friendly imaging technique and protocol for *in-situ* documentation of punch marks, in the form of an *app* connected with an

European stamp database, could guarantee comparable homogeneous results and contribute to provenance questions.

There is a need to identify and study 'pristine' gilt leathers, that are still in their original location, well documented, have had little restoration treatment and have a known production date or provenance. The ideal is to connect the collected archival information with the gilt leather objects or wall hangings and their material characteristics. This large amount of information needs to be collected, structured and organized at least at European level, for example with a shared database. This database could advance current issues of dating and provenance substantially.

MATERIAL DYNAMICS

Knowledge of degradation processes and agents of deterioration are available for each of the materials in gilt leather. Research should focus on both the chemical and physical interactions between the components of the different materials and their degradation products, and on the influence of external factors, such as climatic conditions.

As the study of material dynamics is a potentially vast field, experts have suggested studying the effects of past conservation treatments, such as the use of various oil products or solvents, on historic gilt leathers as a way to make a start in investigating degradation mechanisms. The topic of leather oiling and the effects on silver, varnish and paint layers could lead to an in-depth study of silver corrosion and related degradation mechanisms.

Corrosion of the silver leaf has an ruinous impact on the visual appearance and hence the perception of gilt leather artefacts. Internal and external material factors possibly influencing corrosion are very complex and need to be investigated, such as increased porosity of the organic layers under and on top of the silver foil, acidic tannins in the leather or sulphur or copper containing pigments in the paint. The effect of past conservation treatments with (sulphated) non-drying oils or environmental influences such as atmospheric gaseous pollutants, moist and high levels of relative humidity, and UV-radiation also need further research.

A topic of great importance is the relation between environmental parameters (RH, temperature, pollutants) and the condition of gilt leathers. Studies on the impact of the environment on the conservation of gilt leather are scarce and should be conducted. For degradation studies there is a need to find examples that have a known history of environmental conditions to which they have been exposed. Research should be carried out on objects that are felt to be best preserved through the ages. For example analyses of silvered leathers that have not oxidized will help to understand the material and environmental circumstances needed for preservation and could aid to develop preventive conservation measures.

An illustrated glossary of degradation phenomena will be very helpful for the awareness of material degradations and changes over time. Together with preventive conservation guidelines this can be a first step in improving conservation conditions for these heritage artefacts.

CONSERVATION TREATMENTS

The conservation and restoration of gilt leather objects and wall hangings is complex due to the sensitive nature and combination of organic and inorganic materials. It requires specialized knowledge transcending conservation practices found in individual conservation disciplines. Interdisciplinary collaborations between conservators of different disciplines should be promoted, while safeguarding specialized knowledge dissemination on conservation issues specific for gilt leather.

Specialized knowledge for structural conservation work has already been developed to a large extend, focusing on the development of flexible hanging systems for gilt leather wall hangings. To ensure safety guidelines, further mechanical testing of gilt leather is required (strength, elasticity and elongation of aged gilt leather), as well as studying sorption behaviour and dimensional changes as a response to changing climatic conditions, and as a function of ageing (condition) and manufacturing characteristics (e.g. type of tanning, type of leather, degree of tooling, etc.). An important next step is the monitoring of installed hanging systems, and their effect on the structural integrity of the gilt leathers, by checking deformations, stretching, tears, stress and cracks in the decorative layers. Research is needed to develop micro-analytical non-destructive tests that are comparable with standard test methods.

Furthermore there is still a need for the development of new conservation materials, techniques and methods, such as adhesives for (strip) linings, and advanced cleaning techniques for the decorative surfaces. Other topics that need attention are the development of accessible, easy and portable diagnostic tools for material characterization and damage assessment. The study of the effects of macro- and micro-climates on wall hangings is a subject that also requires further investigation.

Awareness and dissemination of knowledge about the sensitivity of the individual materials within gilt leather is urgently needed, including an overview of past conservation treatments on gilt leather objects. This should be directed towards owners, caretakers and curators of gilt leathers, as well as conservation architects and practicing conservators from different disciplines and students. Experts have suggested a simple digital platform in various languages, that communicates conservation guidelines and the risk of certain conservation materials and treatments, and disseminates best and worst practices from individual conservation cases.

DIAGNOSTICS

For certain material components of gilt leather, such as leather and silver, state of the art diagnostic techniques are being used and methods have been developed for material identification, the characterization of degradation and for condition assessment. For other materials, such as protein-based adhesives and oil-resin varnish layers the appropriate diagnostic techniques have to be selected and tested yet.

Methodologies for the characterization of all the material layers in gilt leather, using multiple analytical techniques, are being developed and should be elaborated. Selecting and testing the appropriate complementary analytical techniques that, when combined, will be able to characterize all different organic and inorganic materials of gilt leather requires time, as testing, measuring and data processing protocols still need to be developed. The challenge is to offer a real integrated approach, where diagnostic development and research questions from an art historical or conservation perspective are both addressed.

The use of high tech analytical equipment (e.g. ion beam accelerator) has proved powerful in delivering information on a molecular level. This should be complemented with other non-destructive diagnostic techniques that deliver information on a micro- and macroscopic scale. The complementarity of various non-destructive imaging and spectroscopic techniques needs to be examined.

Development of diagnostic tools should ideally result in easy to use, portable and affordable equipment that in the long run can serve conservators as well. If equipment cannot be taken out of a laboratory setting, creating accessibility of diagnostic equipment to conservators for the material characterization and condition assessment of gilt leather materials should be enabled.

CONCLUSION

The conclusion of this project is a prioritized research agenda that asks for European and international collaboration. This is acknowledged by all the leading gilt leather conservators and experts, and underwritten by scientists in material dynamics and diagnostics. Different players may take on different research themes or fields. Research data should be collected, shared and organized collaboratively. Aside from this research agenda there is a great need for knowledge dissemination and communication about the degradation and conservation of gilt leathers, that should also be addressed multilingually at an international level.

INTRODUCTION

1 A 17th century Dutch gilt leather wall hanging (Northern Netherlands, 1640-1660) in the 'Grevinnans förmak' of Skokloster Castle, Sweden.

2 Detail of figure 1.
3 Two silvered leather panels of the wall hanging in the 'Brahematsalen' of Skokloster Castle, Sweden.

GILT LEATHER: ENDANGERED CULTURAL HERITAGE

Gilt leather was one of the most fashionable and costly types of wall hangings in the Western world in the 16th to 18th centuries. Despite its appearance, it is not real gold that creates the golden shine, but a silver leaf which is coated with an orange-brown lacquer to obtain a golden lustre. The origins of this particular decorated leather lie in North-Africa (Ghadames, Libya). The craft spread through Spain towards the rest of Europe in the late Middle Ages. As a luxurious wall decoration, gilt leather was placed in interiors in the most important and wealthiest houses and castles, often as a decorative background to important art collections.

In the mid-17th century Dutch gilt leather had a similar fame to Delftware and Dutch paintings. Due to its innovative embossments and fashionable artistic design, Dutch leathers became an international export product. Examples of Dutch gilt leather wall hangings can be found in stately homes and castles worldwide, such as Skokloster Castle (Sweden) (figures 1-3). Further excellent examples are present at Moritzburg Castle (Germany), Villa Aldobrandini Rome (Italy), Highclere Castle (England), Yusupov Palace St. Petersburg (Russia) and even the estate Groote Schuur in Rondebosch (South Africa). Subsequently many international museums have Dutch gilt leathers in their collections, for example the Museo Stibbert Florence (Italy), Victoria & Albert Museum (UK), Musée des Arts Décoratifs (France), Museo Nacional de Artes Decorativas Madrid (Spain), Tokyo National Museum (Japan), and the Metropolitan Museum of Art (USA).

In most European countries only a small fraction of the large amounts of gilt leather wall hangings produced has been preserved. In the Netherlands only 60 gilt leathers have survived *in situ* in historic houses, castles, palaces, churches, town halls and other public or private institutions. This is only a small percentage of what once existed. Archival research pointed out that in Leiden, just on the Rapenburg alone, one of the main canals of the city, 60 rooms were decorated with gilt leather. None of these have survived. Due to the complex nature and sensitivity of the material, conservation of gilt leather is a challenge. Historical craft-led conservation practices, focused solely on either the leather support or the decorative surface layers, negating the fragility of each of the separate materials used. As a consequence a considerate amount of historic gilt leather ensembles and objects are in an alarming condition.

BACKGROUND TO THE PROJECT

In 2013 at the invitation of Dutch gilt leather experts an international group of scientists, conservators and specialists met at Stichting Restauratie Atelier Limburg (SRAL) in Maastricht. At this meeting they discussed the conservation problems and the urgency to preserve these unique works of art. Discussions on the conservation problems pointed out the technical challenges of the mechanical properties, as well as the challenges of chemical degradation mechanisms on a molecular level. Both aspects are not well understood yet, let alone have been related to each other.

The Expert Meeting concluded that analytical research of gilt leather is desperately needed to provide an in-depth understanding of the different material layers, their interactions, and their behaviour to changing climatic conditions. This characterization would be of paramount importance to the development of improved treatment strategies for the conservation of gilt leather. To succeed an integral and interdisciplinary approach is needed. Conservators of different disciplines, art historians, conservation scientists, and engineers should collaborate together to take conservation practice of gilt leathers to the next level.

In 2015 such an interdisciplinary consortium was formed, within the context of the Netherlands Institute for Conservation, Art and Science (NICAS)[1], composed of experts from the Cultural Heritage Agency (RCE), Stichting Restauratie Atelier Limburg (SRAL), Restauratie Nijhoff Asser (RNA), the University of Amsterdam (department of Conservation and Restoration of Cultural Heritage) and Delft University of Technology (departments of Aerospace Structures and Materials (TUD-ASM), and Materials Science and Engineering (TUD-MSE)). This consortium teamed up to define new research directions for the development of improved conservation strategies for gilt leather artefacts, in a project that was funded by NICAS in 2016. This paper is one of the outputs of this Dutch project. It aims to reflect the international state of the art in gilt leather research and conservation, and formulates a shared research agenda for 2017-2025.

As part of the NICAS seed-money project a second international Expert Meeting and Symposium, held in Maastricht on 31st March and 1st April 2016, was organised to further exchange knowledge on the topic, with a focus on bridging advanced analytical research possibilities with conservation and art historical questions. The results of this meeting, with over 60 experts from all over Europe, are included in the white paper. The list of participants is included in the acknowledgements section.

For this project, alliances were built with some of the keepers of gilt leather artefacts in the Netherlands. The Jewish Historical Museum, the Rijksmuseum, the Fries Museum & Museum Princessehof and the Limburgs Museum, Venlo provided access to their collections for the case-studies. During the project preliminary testing was performed on gilt leather fragments of the Rijksmuseum, the Maastricht Town Hall and the Lenghenhofje in Dordrecht. Preliminary non-destructive analyses were performed with hyperspectral imaging (at TUD-ASM) in order to get a better understanding of specific degradation phenomena taking place within the decorative layers.

ABOUT THE WHITE PAPER

The white paper has two main goals: to communicate the state of the art in art historical research, the conservation and diagnostics of gilt leather; to define research directions for the conservation of gilt leather in general and for a future NICAS project specifically. As such it communicates the art historical knowledge that has been gathered up until today, highlights the most important conservation challenges that we are facing at the moment and explains some of the advanced analytical (diagnostic) methods currently available.

The white paper has been structured along the main themes of the NICAS research program: technical art history, material dynamics, conservation treatments and diagnostics.[2] The state of the art in gilt leather research in each of these themes will be presented in the subsequent chapters, followed by an overview of possible future research directions, and concluding with possible research themes for a NICAS project in the period 2017-2021.

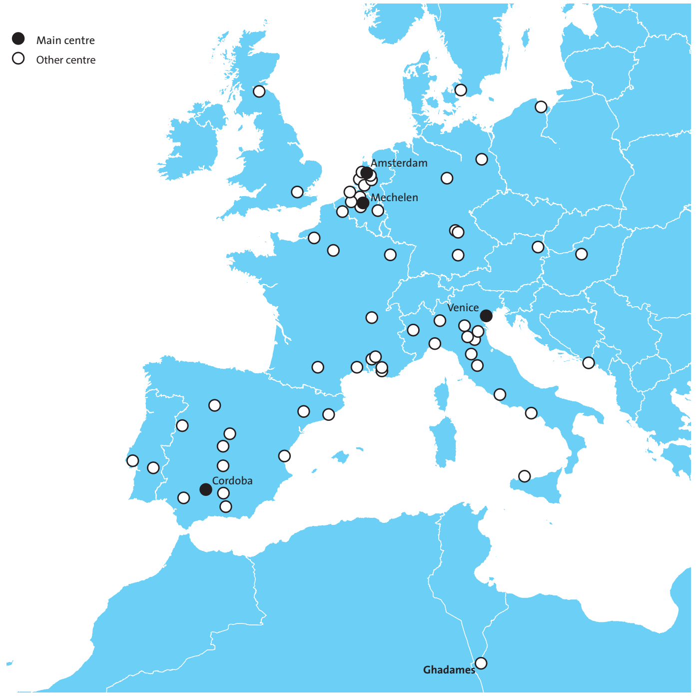
The white paper has been developed by the consortium of the gilt leather project. During the different activities of the project it has served as a discussion document: to raise problems, to work out potential solutions and to get feedback from the international conservation and science community. As such its function is to connect researchers and practitioners from different disciplines and to find common ground.

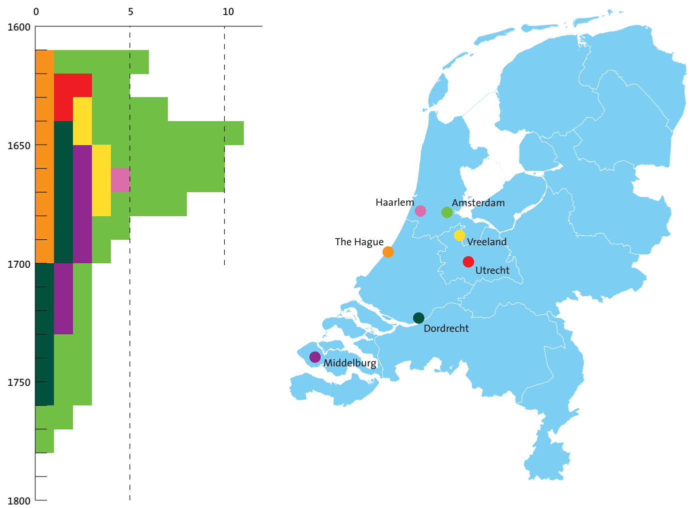
We hope that this white paper will continue to act as a communication tool that stimulates the reader to look again at gilt leather, establishes more appreciation for these important cultural heritage artefacts, creates an understanding of its complexities, encourages interdisciplinary cooperation and motivates in the important task of care of this delicate material.

1 The Netherlands Institute for Conservation, Art and Science (NICAS) is a new innovative interdisciplinary research centre, uniting art history, conservation and science. The Institute, initiated in collaboration with the Netherlands Organisation for Scientific Research (NWO), will work in cooperation with the Rijksmuseum (RMA), the Cultural Heritage Agency (RCE) of the Netherlands, the University of Amsterdam (UVA) and Delft University of Technology (TUD).

2 'White Paper Science for Arts of the Netherlands' by Netherlands Institute for Conservation, Art and Science (NICAS), NWO, 14 december 2015, <www.nwo.nl/en/researchandresults/programmes/ew/nicas/index.html>.

TECHNICAL ART HISTORY





Timeline: (maximum) number of gilt leather factories per place per decade

4 Centres of historical gilt leather production in Europe.

5 The centres of gilt leather production in the Netherlands, with the number of manufacturers in the 17th and 18th centuries. Source: Koldeweij 1998.

CONVENTIONAL ART HISTORICAL RESEARCH

A general overview of the history of gilt leather production in Europe was first described in detail in 1971 (Waterer 1971). Gilt leather for interior decoration has been produced throughout Europe from the 15th till the 20th century. The craft of gilt leather making originates from Northern Africa and was introduced by the Moors to the Iberian Peninsula in the early Middle Ages. As Moorish craftsmen were forced to migrate to other European countries in the 16th century, gilt leather making skills spread further into Europe. Countries with a known history in producing gilt leather are: Spain, Portugal, Italy, France, the Northern and Southern Netherlands, Germany, and England (figure 4). The peak production in Spain and Portugal was during the late middle-ages (until the 16th century), while in France and Italy production was flourishing in the 16th and 17th century. The Northern and Southern Netherlands (figure 5) and England followed slightly later and had their Golden Age in the 17th and 18th centuries.

Depending on the country and city the gilt leather makers were part of the guild system. In Spain they did have their own guild, in many other places (e.g. Venice, The Hague) they resided under the St. Luke guild (Koldeweij 1998). In Venice this resulted in interesting collaborations with painters. The guilds were known to have a regulating function, and as such set production standards, safeguarding a very high quality of the gilt leather produced in the various countries. Cities with several production centres and an extraordinarily high production in the 17th and 18th centuries were Venice, Mechelen, and Amsterdam. In most of these centres the local archives hold important documents regarding this branch of industry with all kinds of relevant information.

Gilt leather was mainly used for decorative wall hangings, but has also been applied in a huge variety of objects, such as folding screens, chairs, chests, suitcases and plaques (Koldeweij 1998). It can also be found in ecclesiastical settings both as altar frontals and as ecclesiastical vestments. Gilt leather adorned the castles and palaces of the aristocrats, churches, board rooms, the houses of the wealthy bourgeoisie and the like. Initially gilt leather hangings had a mobile character and were hung loosely on small leather loops. For storage the gilt leathers were rolled and kept in cabinets. During the seventeenth century only the extremely wealthy could afford gilt leather wall hangings, and they were hung in the grand rooms, often in the dining and large reception rooms. During the 18th century more people could afford gilt leathers, and they were sometimes moved to less prominent places in the buildings. Gilt leathers gained a more permanent place in interiors as they were tensioned and fixed between wainscotings (figures 6-8).

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6 Gilt leather wall hangings (1739) in the board room of the Pieterskerk in Leiden.
7 Chinoiserie gilt leather wall hangings (1739) in the Mayor's room of the town hall of Maastricht.
8 Gilt leather wall hangings (1768, workshop of Johannes Remmersz and Son, Amsterdam) in the board room of St. Pietershof Hoorn.

Gilt leather, whatever its application, can roughly be divided in three types: flat with decorative repetitive patterns (figures 9, 10), embossed with decorative or illustrative or representational depictions (figures 11-13), and lastly flat with painted scenes (figures 14-16). The majority of the wall hangings that have been preserved are of the decorative kind, either flat or embossed. Less known, and rarer are the wall hangings with large painted scenes, depicting mostly landscapes, classical or biblical scenes. Contemporary engravings have been used by gilt leather painters as a source of inspiration. Important examples are in the collection of the Musée de la Renaissance in Écouen (France), in Moritzburg Castle (Germany), Dunster Castle (England), and Drottningholm Palace (Sweden). In the Netherlands a few wall hangings of this type have been preserved, for example the gilt leather with hunting scenes of Paleis het Loo (Apeldoorn) (figures 14, 15) and the chinoiserie wall hangings in the town hall of Sneek (figure 16) and in the Maastricht town hall.

Gilt leathers from the different European countries are diverse, and next to the above mentioned main types, 2 important subtypes should also be mentioned: gilt leather decorated with wool flock (figures 9, 10), and the so-called 'silvered leathers' in which (parts of) the fond has not been covered with gold varnish, and has been left silver (figures 1-3).

The majority of the decorative patterns on gilt leather wall hangings closely followed contemporary stylistic developments in textile design, mostly those of costly silk brocades (Koldeweij 1998). The patterns are either singularly repeated on each individual leather panel, or are designed in such a way that a series of panels form together a continuous motif. In 1628 Dutch craftsmen introduced embossing techniques to create high relief motifs. Driven by the refinement of production techniques, a new artistic morphology for gilt leather was developed, moving away from textile patterns. Designs in the very fashionable auricular style were introduced. Exuberant naturalistic motifs, such as foliage, garlands, flowers, insects, birds and other animals, elegantly covered the whole surface, without a defined orientation. Allegorical or mythological figures were often used, with themes such as the five senses, the four seasons, the four elements and vanitas symbols (figures 11-13). This renewed gilt leather was in great demand, both inside and outside the Netherlands. By the end of the seventeenth century designs underwent a change in style. Patterns became symmetrical, the embossments diminished and subsequently disappeared, patterns again began to mimic textile designs. This reflected the French influence in the decorative arts and in architecture at the time.

In a limited number of countries detailed art historical research has deepened the knowledge about gilt leathers. In France, the Netherlands, Flanders, Germany and parts of Italy, an inventory of the preserved gilt leathers has been made, including classification

9 The Hechal with open doors, showing its original gilt leather lining, in the Portuguese Synagogue, Amsterdam.

10 The gilt leather lining is decorated with a flower pattern in wool flock (1675, Southern Netherlands).

(iconography, decorative patterns and ornaments), (stylistic) dating and provenance (Bergmans and Koldeweij 1992, Koldeweij 1998, Bärnighausen 2004, Fournet 2004, Nimmo et al. 2008). Archival research has given an insight into the manufacturing of gilt leathers in the Northern Netherlands, while there is a reasonable view of production in Spain, the Southern Netherlands and England (Madurell i Marimon 1972, Bergmans and Koldeweij 1992, Koldeweij 1998 and 2000). The gathered information describes the number of workshops present in the subsequent centuries, the materials they were using, tools and production methods, the organization of the workshops, the selling, distribution and the export of gilt leathers. Archival research has also brought to light contextual information about the use of gilt leathers in interiors: the type of buildings they were used in, which rooms, how they were hung, their value, and their relation to other interior decorations (Koldeweij 1998). However for the majority of European countries that had an important gilt leather manufacturing, this type of archival research still needs to be undertaken. In Italy and France for example important archival information awaits to be studied (Bonnot-Diconne 2012).

Despite the information that has been acquired through archival research, the determination of date, provenance and attribution to workshops remains a challenge. With only one or two exceptions, manufacturers in the Netherlands did not sign, mark or date their gilt leather products [This in contrast to Spain, where in most cities the guilds introduced a stamp with the city arms, that guaranteed the quality of gilt leather products. Some of the preserved Spanish leathers contain this logo (Koldeweij 1998)]. Although in the mid-17th century some of the pattern designs of the printing plates were patented, successful designs were nonetheless copied by workshops, even across European boundaries. It has proved rather difficult to assign preserved gilt leather artefacts and hangings to specific workshops.

Production technology

In addition to archival research, the study of historical technical sources has also yielded important information on the production process of gilt leather. The most elaborate and important description of the making of gilt leather is *Art de Travailler les Cuirs Dorés ou Argentés* by Fougeroux de Bondaroy for the series *Descriptions des Arts et Métiers* of the *Académie Royale des Sciences* published in 1762. Included are two illustrations showing not only the different steps in the production, but also the tools that were used for it (figure 17). Most of the encyclopaedic descriptions on the techniques of gilt leather making of later dates are based on the work of Fougeroux de Bondaroy, including the one in the supplement of the well-known 18th century *Encyclopédie ou dictionnaire raisonné des sciences, des arts et des métiers* of Diderot and d'Alembert (1776). Another source containing valuable information on materials and recipes for paints, glazes and varnishes used in gilt leather production is the manuscript *Secreetboek van Schoone diverse ende eerlijcke konsten* (here-

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11 Gilt leather panel with its corresponding top border, depicting the four seasons (Northern Netherlands, 1640-1660), Collection Deutsches Ledermuseum/Schuh-museum Offenbach, inv.no. 2572.

after *Mechelse Secreetboek*). It was written by the members of the gilt leather makers family Vermeulen from Mechelen (Flanders) over the course of the late 17th and 18th century (Koldeweij 1998, Schulze 2011).

From these sources we get a detailed picture of how gilt leather was produced. They describe the raw materials, how they were manipulated and the tools that were used. In general the production of gilt leather can be described as follows (Schulze 2011) (figures 18-27). The leather, either calf-, sheep-, pig- or goatskin, would be bought ready tanned. In the Netherlands calfskins were preferred because of their compact fibre structure and relatively low fat content (Koldeweij 1998). The quality of the leather was of utmost importance. The skins were first soaked and rinsed to take out any unbound tannins. To increase the flexibility of the leather it was then beaten on stones. The leather was subsequently stretched and the surface smoothened with a blunt metal tool. Sometimes the leather was thinned on the flesh side. The skins were cut to the right size, for which either wooden frames or tables with integrated measures or rulers were used. Weak points and gaps, due to the shape of the hides, were filled in with small pieces of leather, using parchment glue.

Silver leaf would then be adhered with parchment glue to pre-wetted leather vellums (figure 18). In the early literary sources (before 1500) adhesives such as egg white and gum arabic are mentioned. Two layers of parchment glue were applied to the leather with bare flat hands, with a drying pause in between. Then the silver leaves were carefully dropped onto the surface and dabbed with a fox tail. In order to avoid deformations and tension under the silver leaf, the leathers would be tensioned on a wooden frame and left to dry. The silver was polished on a smooth stone surface with a burnishing stone when the leather was still partly moist (figure 19). The resulting amount of gloss is dependent on the surface structure of the leather, as well as the thickness of the silver leaf. Compact leather fibres and thick silver leaves render a high degree of gloss. Some literary sources mention the application of egg white or parchment glue to protect the silver from tarnishing. Most sources however indicate that the gold lacquer was applied directly on the silver.

The polished silver leaf was subsequently coated with a yellow- or orange-brown oil-resin varnish creating the golden lustre, and therefore often referred to as gold varnish or gold lacquer (figure 21). The production of a properly drying gold varnish with the right colour was not easy and recipes were often kept secret. However from research on historical sources (Schulze 2011) it is known that most recipes mention a linseed oil, heated with different metal components to improve the drying properties, to which a variety of natural resins were added, such as sandarac, colophony or turpen-tine balsams, and sometimes gum resins, or mastic, and different

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12 Gilt leather panel, depicting Hercules (Amsterdam, 'De Vergulde Roemer' or 'De Gecroonde Son', 1640-1660), Collection Deutsches Ledermuseum/ Schuhmuseum Offenbach, inv.no. 8282.

13 Fragment of a gilt leather panel showing the extreme refined details of a Dutch gilt leather (Northern Netherlands, 1670-1680), Collection Rijksmuseum Amsterdam, inv.no. BK-18267.

14 The panel with the stag hunt of a huge gilt leather wall hanging (1650-1700, Southern Netherlands), located in Paleis Het Loo, Apeldoorn.

15 Detail with a bear hunting scene on one of the other panels of a huge gilt leather wall hanging (1650-1700, Southern Netherlands), located in Paleis Het Loo, Apeldoorn.

colouring components, e.g. saffron, aloe, cochineal, gamboge or dragon's blood, depending on the region of produce. The use of amber and asphalt can be considered specific to the Netherlandish gilt leather workshops. The oil-resin varnish was applied with bare hands in s-shaped motions, and then tapped with flat hands to spread it equally over the surface. Usually two layers of the coloured varnish would be applied, and left to dry outside in the sunlight.

After the application of the varnish the gilt leather was ready to be decorated. In the case of flat punched gilt leathers, underdrawings were made to mark the outlines of the decorative design (figure 20). Metal or wooden printing plates are mentioned in literary sources, but the decorative design could also be transferred by pouncing, or stencils, and in the case of unique patterns it could even be hand drawn. For embossed leather this was not necessary as the embossing already marks the outlines of the design.

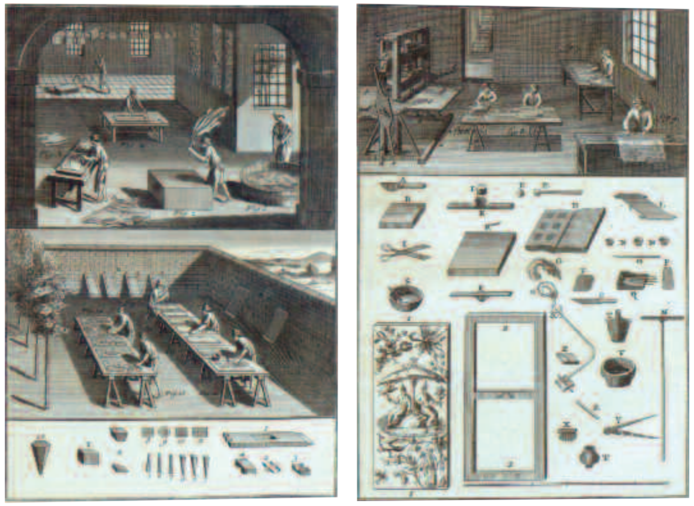
Embossing, a technique to create raised relief patterns, patented by Dutch gilt leather makers in 1628, was applied by pressing the 'gilded' leather in wooden or metal moulds and counter moulds by means of different types of presses, similar to those used for printing (figures 22, 23). The leather would generally be wetted on the 'flesh' side with a sponge before pressing.

The decoration was then completed by painting floral or other decorative motives with the desired colours, by the use of glazes and oil paints (figure 24). Occasionally specific parts were selectively coated with a spirit varnish to create glossy effects.

One of the last phases of workmanship for the flat decorative gilt leathers was the punching of repetitive patterns of geometrical shapes onto the parts of the design that would be left unpainted (figure 27). A large variety of metal hand punches in diverse sizes were available (figure 26). Depending on the workshop the stamps were either applied before painting and glazing, or after (Schulze 2011). It was not common practice to provide embossed gilt leather with punch marks. However examples that combine the two techniques do exist.

In the case of decorative wall hangings the singular rectangular gilt leather panels would be sewn together after decoration. In the 17th century, long vertical planes of gilt leather without horizontal seams became fashionable for coverings with large painted scenes. In the 18th century, this style would also become fashionable for decorative gilt leather wall hangings. The leather rectangles were joined together by first pairing the leather and then glueing the separate panels together. There are even examples of large wall covering surfaces without any seams (figure 16). In the Netherlands this was done before the silver leaf was applied. In England however examples have been found where the panels were glued after the silvering (Koldeweij 2000).

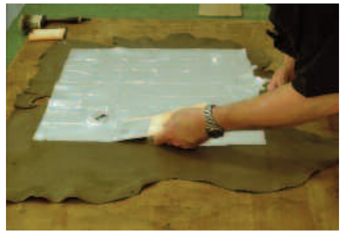
TECHNICAL ART HISTORY

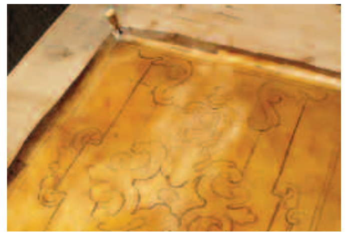


16 Chinoiserie gilt leather wall hanging (without horizontal or vertical seams) depicting the five senses (1760-1764), located in the board room of the town hall of Sneek.

17 Different steps in the gilt leather production process depicted on engravings from Fougeroux de Bondaroy 1762.

TECHNICAL ART HISTORY

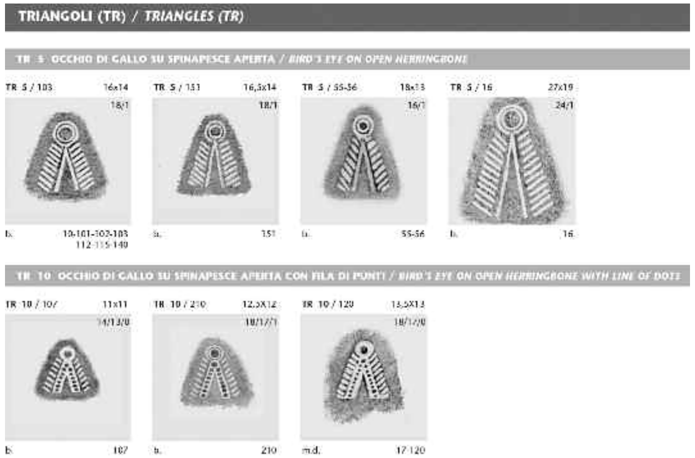




Different steps in the making process of gilt leather. Experimental reconstructions by Andreas Schulze, 2011.

18 The application of the silver leaf.
20 Application of the outlines of the design.
22 Embossing of the 'gilded' leather by means of a wooden mould and press.
24 Painting the lower parts of the design.
26 Reproduced stamps.

19 Polishing of the silver leaf.
21 The gold varnish is applied with flat bare hands.
23 Embossing of the 'gilded' leather by means of a wooden mould and press.
25 A flat gilt leather before punching and painting.
27 Punching of a flat gilt leather.



28 Different punch marks on one of the Italian gilt leather wall hangings of Schloss Moritzburg, Germany.

29 The 'birds eye on herringbone' punch mark characteristic for Italian gilt leather (not traced in other countries), transferred onto paper for documentation.

30 The 'birds eye on herringbone' punch mark on one of the Italian gilt leather wall hangings of Schloss Moritzburg, Germany.

TECHNICAL ART HISTORY

Technical art history is a relatively new approach that has gained ground over the past ten years. The emphasis is on technical analysis of the materials of the art work, and the fabrication technology is studied by making reconstructions by following recipes from historical literary sources. Combining the information gathered from material characterization of art works, reconstructions of historical recipes from art technological sources and archive research, results in new insights for both art historians and conservators.

Until recently technical examination of materials was only done within the context of individual conservation projects. Recently however in France, Germany and Italy, research projects have started that take a systematic and integrated approach to materials characterization and the production technology of gilt leather. This focus is on the characterization of all the materials that gilt leather consists of, not only to get a better understanding of the production technology, but also to identify distinctive characteristics that will aid in determining fabrication date, geographical provenance and attribution.

Leather and animal species

One aspect that could be used to determine geographical provenance is the type of leather that was used for the gilt leather. In the Netherlands mostly calf hides were used, both from France (Limousin cow) and from Friesland (Frisian cow) (Koldeweij 1998). Both species were known for their excellent quality. Spanish gilt leathers are usually made of goat skins, which were also of high quality. Less stable were the sheep skins, which were used in France, Italy and Spain, next to the more commonly used goat leather. Historical research would be helpful to get a clear understanding of all the sources of leather for gilt leather production, to understand tanning and skins used.

The animal species can normally easily be determined by examining the hair implant on the grain side of the leather. However on gilt leather this is not possible, as this side is completely covered with decorative layers: the metal foil and the varnish and paint layers. With advanced mass spectrometry techniques the species can be identified (Kirby et al. 2013). An accessible tool or analysing technique for identifying the species and even the specific type/breed would be of benefit for conservators.

Silver leaf

Systematic material characterization of gilt leather has recently been started by a French consortium. Forty-five different samples of Italian and French gilt leather from the 16th-18th century have been analysed with different analytical techniques, in order to determine the composition of the characteristic materials for gilt leather: the leather itself, the silver leaf and the oil-resin varnish (Bonnot-Diconne 2012, Radepont et al. 2015). Within this integrated approach the emphasis is however on the analysis of the silver leaf: chemical composition, thickness and dimensions. It is hoped that

31 Fragment of a gilt leather wall panel in normal and UV-light. The UV-fluorescence clearly shows the selective application of (an original) varnish.

33 Glossy effects of the original varnish layer on the green foliage.

32 Glossy effects of the original varnish layer on the parrot's feathers.

All photo's taken during a pilot restoration at SRAL in 2015 of one of the panels of the gilt leather hangings of the board room of the Lenghen-hofje Dordrecht (1760-1765).

from these data chemical or physical markers for geographical provenance can be derived. The first results are promising, however for reliable judgements, a much larger reference group of gilt leather samples is needed, preferably with a known date and provenance. An international database would be highly desirable.

Gold varnish

Schulze has undertaken an in-depth study of historical technical sources on gilt leather (Schulze 2011) and reconstructed some gold varnishes according to the historical recipes he found. Technical sources indicate that the ingredients of the 'gold varnish' vary from region to region. Schulze found 55 different varnish recipes in 27 sources. In order to find out whether regionally specific 'colouring' ingredients in the 'gold varnish' could be identified, Schulze analysed the material composition of Italian and Dutch gilt leather wall hangings of the baroque Schloss Moritzburg (Dresden, Germany) with GC-MS (Schulze 2011). He compared the outcomes with measurements of reconstructions (models) with known components. The main ingredients such as the linseed oil, and the type of natural resin used, such as sandarac, colophony, copal, mastic, and turpentine could readily be identified using gas chromatography mass spectrometry (GC-MS). Colouring components however, such as asphalt and saffron, were more difficult to detect. This has recently been confirmed by measurements of French researchers (Robinet 2015). Other analytical techniques, such high-performance liquid chromatography (HPLC) and Mass Spectro-metry Imaging (MSI) should be explored.

Punch marks

Punch marks are another characteristic of gilt leathers that can potentially be connected to specific countries, regions, cities, and perhaps even workshops (figures 28-30). The flat 'gilded', and in some cases embossed, leathers are decorated with stamps of punches with a large variety of different geometrical patterns, such as circles, squares, diamonds, triangles, dot patterns or parallel lines. Together they create a play of reflected and scattered light in the decorative design. Often the various punch marks were used to articulate the painted patterns. In some of the gilt leathers with painted scenes they have been applied for instance to simulate the texture of garments.

Typical punches have been described in different historical sources: e.g. a short steel stem with a design engraved on one end (Nimmo et al. 2008). It should be placed perpendicular to the surface and tapped sharply (with a hammer). The tools used for the punching of gilt leather were similar to the ones used for book-binding, and most likely they were also similar to the ones used for the stamped decorations of panel paintings. They were produced in specialized metal workshops.

Nimmo, Paris and Rissotto proposed a classification for the different punch marks and published (Nimmo et al. 2008) an inventory of the ones traced on gilt leathers from different regions

34 A female figure painted on gilt leather, fragment of a larger composition, Italian 16th century. Collection Mauritshuis, The Hague, inv.no. MH0349.

35 Detail of the red dress and ribbon: sgrafitto revealing the gold varnish underneath.

in Italy (Lazio, Tuscany and Umbria). A documentation protocol was developed and included in an artefact survey report form. The recording of data on punch marks – for which a database was proposed by Bonnot-Diconne and Paris in the Offenbach ICOM-CC interim meeting (Paris and Bonnot-Diconne 2012) – could lead to the designation of different stamps to certain countries and cities, as metal workshops may have made stamps with a distinct design and size. A comparison of different stamps will lead to an overview of the development of different stamp patterns over geographic areas and time.

Oil paints, glazes and painting techniques

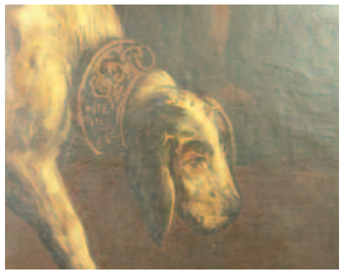
The type of pigments and binding media that were used to make the paints to decorate gilt leather are similar to those used for contemporary easel and panel painting. Little research so far has been done on paint formulations, techniques and workshop practices. Recent findings however indicate that this is an important area of research that can yield new information on the intricate use of binding media to obtain certain painterly effects.

Research has been done on the painting techniques either on decorative, and on gilt leathers with painted scenes (Schulze 2011, Ioele et al. 2011). From source research it is known that some painted parts were coated with a varnish for a glossy effect and other parts were left unvarnished to leave them matt. Historical recipes indicate that glazes, transparent paints made with organic pigments, were extensively used. Often natural resins were added to these paints to increase gloss (Schulze 2011). The Flemish manuscript *Mechelse Secreetboek* is an important source on the use of coloured varnishes that should be disclosed and studied further.

Recently SRAL discovered that on the gilt leather wall hangings of The Lenghenhofje in Dordrecht some of the painted decorations were partially varnished to create a refined play of glossy and matte areas (figures 31-33). An examination of the painting techniques of Knowsley Hall's Venetian gilt leathers (mid-17th century), depicting old testament scenes, pointed out that the gold varnish was used as a middle tone (figure 39) (Posthuma de Boer 2013). In these gilt leathers glazes were used such that the golden ground could shimmer through. Another observed painting technique there is sgraffito. The painter carved away the upper paint, to expose the underlying 'golden' ground (figure 38). All of these techniques have been observed in the gilt leathers of Knowsley Hall (figures 36, 37). Sgraffito has been applied as well on a recently discovered 16th century painting on gilt leather at the Mauritshuis (figures 34, 35).

The above-described painting materials and techniques have not yet been studied systematically. They however determine very much the way gilt leathers were intended to look. Unfortunately in the past restorers were unaware of these painterly subtleties. In their ignorance they have applied restoration materials and techniques that may have altered the appearance of the original

TECHNICAL ART HISTORY



34 The Grand Staircase at Knowsley Hall (UK) showing Borgognone's paintings on gilt leather of 'The Passage of the Israelites into the Promised Land' (whole view) and 'The Crossing of the Red Sea with the Destruction of Pharoah's Army' (partial view), painted in Venice in 1656.

35 Jacques Courtois, known as Giacomo Borgognone, 'The Passage of the Israelites into the Promised Land', oil on gilt-leather (pre-conservation in 2015).

36 Detail showing the technique of sgraffito on the dog collar.

37 Detail showing the gold varnish that is used as a middle-tone (showing grey-brown on the photo).

materials. A better understanding of the characteristics of the used paints, glazes and varnishes, as well as the painting techniques, and the intended subtle effects in the play of light for matte and glossy effects, will eventually lead to better informed restorations, and will improve the presentation of gilt leathers.

CONCLUSIONS

Archival research and state of affairs

The past twenty years research by art historians and conservators has delivered many new facts and figures. These researches have been published in an ad hoc manner in various articles and unpublished theses. A published update of the international state of affairs from the art historical perspective is highly desirable. Next to this, further in-depth archival research of gilt leather is still needed, including the study of inventories, contracts, guild regulations and manuscripts, in the most important production centres of gilt leather in Europe. The archives of several of these cities, such as Venice, Florence, Rome, Cordoba, Seville, Paris and Brussels, have hardly been explored, and will beyond any doubt yield a lot of new information on gilt leather, its production and use.

Technical art history

In the past ten years important advances have been made in the art technological study of gilt leather. Literary sources have been studied extensively, combined with reconstructions and research on the layer built up and material characterization of a select part of gilt leather collections. A start has been made in developing an analytical methodology for integrated material characterization of gilt leather. A small group of gilt leathers with a known date and provenance has been analysed. Most research initiatives are directed towards understanding the production or fabrication processes and eventually determining attribution, geographical provenance and dating.

Leather

So far, little research has been done on the leathers used for gilt leather production, or on (the type of) tanning processes employed. Some material characterization has been performed on gilt leathers to identify the animal the leather has been made of. However it would be interesting to find out more about the animal breeds. This will definitely be of help in determining provenance. What is known so far about the leather and hide selection by gilt leather workshops is derived from literary and archival sources. It would be useful to find appropriate analytical techniques and to develop a methodology for the analyses of the leathers and tanning materials used for gilt leather.

TECHNICAL ART HISTORY

Silver foil

A methodology has been developed for material characterization of the silver foil, that could eventually help to determine provenance and dating of gilt leather. The fabrication process of the silver foil itself has been studied, as well as the handling and manipulation during gilt leather production and its effects on the properties of the silver leaf as we perceive it now. For a tiny group of gilt leathers with a known date and provenance, chemical composition, thickness and dimensions of the silver leaf has been examined. This work should be expanded and continued on a larger scale.

Adhesives and protective coatings

No particular analytical work has been done at all on the protein adhesives used for adhering the silver foil, nor on the materials that have been used as a protective coating on top of the silver. Some 'silvered' leathers are in extremely good condition, such as the ones in Skokloster Castle. This specific type of gilt leather still needs to be studied and analysed, which could also contribute to a better understanding of the degradation and tarnishing processes, and the use and function of protective coatings.

Gold lacquers

The thorough research of Schulze into historical recipes of gold lacquers is promising and offers new information. Gold varnishes can generally be classified by region as they have specific colouring components. Protocols for the reconstruction of oil resin varnishes have been developed, with the aim of establishing reference materials for further analytical work. Attempts have been made to detect the trace components mentioned in historical recipes with analytical techniques. For most of the 'colouring' ingredients the appropriate analytical techniques still need to be found and a methodology needs to be developed.

Punch marks

An initial study of the literary sources on the tooling of gilt leather has been performed and protocols for the documentation and classification of stamps has been developed. Stamps on gilt leathers from three provinces in Italy have been collected. A European database of stamps found on gilt leather has been proposed. New optical 'reading' techniques, such as 3D-surface profiling by means of lasers, combined with updated software for automated identification, will offer opportunities for both faster registering, identification, classification and comparison. The development of an easy to use technique for *in situ* documentation would provide significant advantages and could guarantee comparable homogeneous results.

Pigments, glazes, binding media

Historical paint recipes related to gilt leather production have been studied, and some reconstructions have been made. Results indicate that optical properties of different pigments and binders were known and used to create specific visual effects. The almost inaccessible Flemish manuscript *Mechelse Secreetboek* is a very valuable source on 17th and 18th century paint formulations that needs to be disclosed and studied.

The study of the paint layering on both Italian and Dutch gilt leathers confirms the extensive use of semi-transparent paints (glazes), that were covered with a local varnish, and often used in juxtaposition with more opaque and matte paints. More research needs to be done into the type of pigments and binding media, as well as in painterly techniques, on actual gilt leathers. This should be complemented with the reproduction of recipes from historical sources. Not only will this increase our knowledge about how these works were supposed to look, it will also better inform future conservation decisions. And lastly the reconstructions can be used as reference materials for analytical work, and could be used to study degradation processes.

Both art historical and art technological research has yielded a large amount of archival information and analytical data from artefacts that needs to be structured and combined, at least at European level. A shared database could advance current issues of dating and provenance substantially.

RECOMMENDATIONS FOR NICAS

Connecting study of literary sources, material characterization of objects, and reconstructions

To improve future conservation, presentation and appreciation of gilt leathers it is important to get a better understanding of what newly produced gilt leathers must have looked like. We need to expand our knowledge about source materials and the manufacturing techniques of gilt leather from different countries by additional archival research. To complement the study of literary sources, further material characterization of the actual gilt leather objects and reconstructions of historical recipes is needed. The crux is to connect these different types of research.

Study pristine examples of gilt leather and their context

An important first step should be to carefully select examples of 'pristine' gilt leathers that are still in their original location, well documented, have had little restoration interventions and have a known production date or provenance. Some examples that can already be mentioned in this respect are the gilt leather wall hangings of the Portuguese Synagogue, Skokloster Castle, Lenghenhofje Dordrecht, fragments in storage of Museum De Lakenhal and gilt leathers of the Tokugawa Art Museum, Japan. For these cases there is a high probability that the collected archival information can be connected with the gilt leather objects or wall hangings and their material characteristics, and their physical context. Gilt leathers that are known to be produced in Mechelen should be considered as well, as these can be connected with the *Mechelse Secreetboek* manuscript and additional archival research in the State Archives in Brussels.

Integrated research of all material layers and collaborations using analytical techniques and methodologies

Within the scope of NICAS an integrated research on all material layers of gilt leather should be chosen, collaborating with running research projects to promote efficiency of resources and knowledge exchange. For each material layer – leather, protein adhesive, silver foil, protective coating, gold varnish, paints, varnishes – state of the art analytical techniques and methodology should be addressed. For example for the characterization of the silver foil collaboration should be sought with the French CORDOBA consortium. For other material layers, such as the protein adhesives and the gold lacquer, appropriate analytical techniques need to be selected and methodologies need to be developed. A collaboration with the NICAS project *Organic polymers on metal* should be sought.

MATERIAL DYNAMICS

40 Three tropocollagen helices coiled together to form the collagen molecule.

41 Fibrils and fibril bundles of collagen.

Gilt leather is a layered composite of organic and inorganic materials. The ageing of gilt leather is characterized by the specific degradations of each of the materials and the possible interactions between them. Typical chemical and physical damage and degradation processes have been studied for each of the materials – leather, animal glue, silver leaf, varnish, oil paint – within the literature of the different conservation disciplines: leather, metals and paintings conservation. For example, much has been published on the complex ageing of leather, as well as the degradation of oil paint. However, little literature exists on the specific degradations of the composite materials of gilt leather. Only recently some projects have started taking into account possible interactions between the different materials and degradation products. This chapter briefly describes the material characteristics of each of the layers of gilt leather, and subsequently gives an account of the state of the art of research into the ageing of these materials.

THE LEATHER SUPPORT

Gilt leathers were made from different types of animal hides – calf-, goat- or sheepskins – depending mostly on the country of origin. Animal skin consists of collagen molecules that are made up from approximately 20 different types of amino acids (Kite and Thomson 2006). The collagen molecule is formed by three polypeptide chains that are coiled together in a helix (figures 40, 41). These molecules are organized in helical coils to form a fibril. Fibrils in their turn are again coiled in bundles, resulting in the fibrous structure characteristic of the animal skin. The spatial structure of polypeptide chains is often referred to as a triple helix. Each animal species, and types within species, has a different characteristic fibrous structure, accounting for different mechanical and esthetical properties of the leather.

To make a raw skin durable, resistant to water and bacterial attack, a chemical process called tanning needs to be applied. Before the hides can actually be tanned, they are pre-treated with various chemicals, lime amongst others, to extract water, and all non-fibrous components, such as epidermis, hairs and fat (Kite and Thomson 2006). Then a tanning agent (a tannin) is allowed to react with the reactive groups of the collagen molecule in order to change its structure, improve hydrothermal stability and to slow bacterial breakdown. Until the 19th century vegetable tanning was most common. Acidic extracts (polyphenols) from plant products were used, such as oak bark, chestnut, sumac and myrobalans. Depending on the type of vegetable tannin used a condensation or a hydrolysis reaction takes place. Leathers that are tanned with condensed tannins have proved to be less stable over time (mostly 19th century leathers). Research has pointed out that for the production of gilt leather mainly hydrolysable tannins have been used (Schulze 2011). After tanning, the leather was treated with oil or fat products to enhance its flexibility.

The degradation of leather has been studied extensively by the British Leather Confederation, The Canadian Conservation Institute, The Leather Conservation Centre in Northampton (UK) and The School of Conservation, Copenhagen (Denmark). The fundamental causes of historic leather deterioration were studied on a physical and molecular level, as well as the effect of environmental conditions on leather of different tannings. Two European research projects: STEP Leather project (1991-1994) and the ENVIRONMENT leather project (1996) made important advances in identifying and quantifying chemical and physical changes in historical and naturally aged vegetable tanned leather caused by environmental factors, including air pollution. Within the STEP Leather project the correlation between natural and artificial ageing of vegetable tanned leather was studied with the goal of establishing parameters and protocols for the artificial ageing of leather. The ENVIRONMENT project further investigated deterioration processes in leather and tested the artificial ageing protocols developed during the first project.

The above research has shown that degradation processes within leather are complex, and occur on different levels (Florian 2006). Degradation may be caused by environmental conditions, by components of the tannin-collagen complex itself, by chemicals introduced during pre-treatment of the hides (for example polluted salts), during tanning (metal salts) or during the processing afterwards (oils, fats, dyes). The two most important break-down processes are acid hydrolyses and oxidation, which take place both within the collagen molecules and within the bound tannins. Hydrolyses of vegetable tanned leather takes place under the influence of oxygen, sulphur- and nitrogen dioxide in ambient air. Sulphur dioxide may be transformed to sulphur trioxide by sunlight, which may react with the tannins to form sulphuric acid. Oxidation processes are triggered by light, ozone, oxygen and oils, and also by pollutant gasses (sulphur dioxide). The collagen structure is broken down under the influence of free radicals, or hydrolyses, by processes of chain scission, cross-linking and the formation of small polymer fractions. Peptide chains are broken down into amino acids, which in their turn are broken down into ammonia. Degradation processes are influenced by the environment within the leather, such as water, heat, light, pH and gasses. To further complicate the process, components of the tannin / collagen complex itself can be agents of deterioration as well. Tanning agents undergo oxidation and hydrolyses processes, and the resulting degradation products in their turn stimulate oxidative and hydrolytic breakdown of collagen fibres. Condensed tannins, such as mimosa and quebracho, absorb more oxygen and degrade faster as a result. Metal complexes can act as catalysts in reactions which result in sulphuric acid. The above described degradation processes result in depolymerisation and a reduced cohesion of the leather fibres, a lower mechanical strength, a lower pH and a change in colour. It is found that the degree of deterioration, the degree of oxidation and hydrolysis, correlates to the hydrothermal stability of the material (Larsen 2000).

The value of using test samples with known provenance and an understanding of the conditions under which they have been exposed was crucial to the success of the STEP and ENVIRONMENT leather projects. At the core were historic leather samples of a known manufacture from the 1920's which had been used to bind books in two libraries with contrasting environments, namely London (UK) (polluted) and Aberystwyth, Wales (clean). The difference in condition was fundamentally due to the difference in the levels of pollution in the two environments. As part of the STEP and ENVIRONMENT leather projects degradation products of both collagen and tannins have been identified and quantified, and as a result degradation mechanism are now better understood.

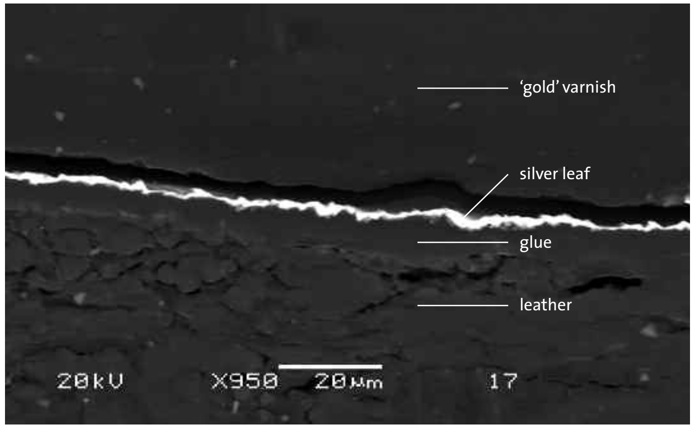
THE DECORATIVE LAYERS

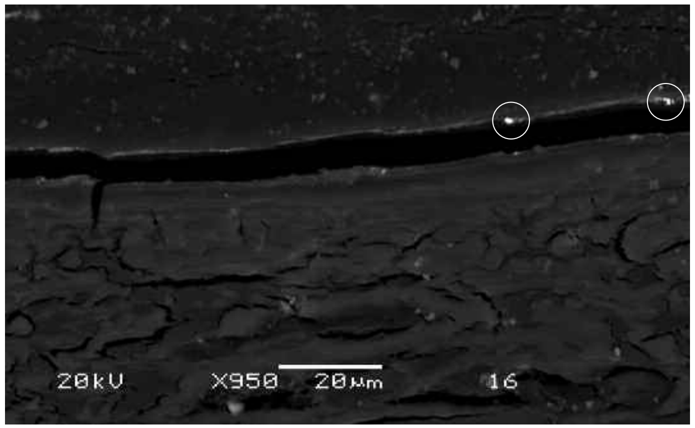
Silver leaves

Silver reacts with reduced-sulphur containing compounds, e.g. hydrogen sulphide, carbonyl sulphide in the air, or with elemental sulphur (Selwyn 2004). The reaction product silver sulphide appears in different colours, e.g. yellow, red, blue, or black depending on the thickness of the film. When silver is exposed to an environment containing chloride ions, such as in coastal regions or in exposure to human skin, it forms silver chloride.

Tarnishing of the silver leaf of gilt leathers is a much observed degradation phenomenon. It has been described and characterized on a macro- and microscopic level. However tarnishing compounds and reactions have not been analysed yet. An in-depth study of the exact degradation mechanisms of the silver tarnishing, the interaction with degradation products of other materials in the gilt leather, and the influence of climatic conditions has not been performed yet. Nor has the evolution process of the tarnishing been studied. There may be parallels to corrosion processes on photographic gelatin silver prints.

Visual changes in the appearance of the material on a macro-level have been described. Often silver tarnishing appears around the zones that have been decorated with punches (figure 42). It can be seen regularly as well in zones where different silver leafs overlap. It shows as a local darkening (brown, green, grey) or even blackening of the surface. This damage can be related to the production of gilt leather. As the punching has been applied after the application of the gold varnish, it has damaged the varnish coating locally. Ambient air can access the silver leaf and a tarnishing reaction occurs. The degree of tarnishing depends on the degree of damage of the varnish layer, which is a direct result of the depth of the tooling. Tarnishing may also occur due to embrittlement and micro-cracking of the oil-resin varnish caused by light exposure (Schulze 2011). Increased tarnishing has also been observed on parts of the leather that have been skived and glued together to create large panels. Tarnishing may also have been induced by certain unbound tannins in the leather, and may appear quickly after the production (Schulze 2011).





42 Brown areas around punch marks: a result of silver tarnishing. Detail of the gilt leather wall hanging (1768), Sint Pietershof Hoorn.

43 SEM-BSE image of a cross-section of an untarnished sample: white line indicates silver leaf. Gilt leather Sint Pietershof Hoorn.

44 Cross-section of a tarnished sample: only remnants of silver leaf remain. Gilt leather Sint Pietershof Hoorn.

Tarnishing has also been observed that has no direct relation with the production process of the gilt leathers, but rather with environmental conditions, such as an excess of moisture (Posthuma de Boer 2012). This also shows in darkening, blackening, and browning of a surface that should normally be gold coloured. Tarnishing has also been related to the presence of certain restoration products, such as oils and waxes, which have been applied in previous restorations (Posthuma de Boer 2012). It has been suggested that these organic substances may dissolve corrosion products. In these cases the silver leaf is not visible anymore on a macro-level, and the brown leather becomes visible, which correlates with the absence of silver on a microscopic level (figures 43, 44).

In a study of Talland et al. the elementary composition of the silver leaf of gilt leathers of different provenances has been analysed with Proton Induced x-ray Emission (PIXE, performed with a particle accelerator) (Talland et al. 1998). The Dutch and Flemish gilt leathers had a considerately higher amount of lead, than the Italian and Spanish ones, which had higher silver contents. This research focused on tarnishing that occurs on parts of the silver leaf that had intentionally not been covered with the 'golden' varnish, to create a visual play between silver and gold reflections. Corrosion processes, as well as migration of corrosion products into the organic layers have been observed. Possible causes that were mentioned are gaseous pollutants, light sensitivity of the silver, the composition of organic layers that had been applied on the silver during restorations, and acidic (leather) and humid environments. Suggestions for further research are to determine whether corrosion products are migrating towards the leather, or into the organic layers, and to determine the influence of light in the rate of tarnishing processes.

There are many factors that may induce or enhance the corrosion processes of the silver leaf in gilt leather. Observations of conservators also point to possible reactions with sulphur containing pigments, such as orpiment (see figure 60) or vermilion, or reactions with copper containing pigments, such as verdigris or copper resinate (observations by Bianca van Velzen, SRAL, 2015). It has also been suggested that metal siccatives (e.g. lead particles) present in the oil-resin varnish may be of influence on corrosion processes. None of the above mentioned possible factors influencing corrosion processes have been analysed systematically yet.

Recently a research project CORD'ARGENT has started by a French consortium (Radepont et al. 2015). It concentrates on the degradation of silver leaf in gilt leather. Certain characteristics of the silver leaf, such as composition, thickness and surface roughness, have been analysed with PIXE and Rutherford Backscattering Spectrometry (RBS, performed with an ion beam accelerator), on 45 different historic gilt leathers from 16th-18th century. These characteristics are a direct result of the manufacturing process of the silver leaf, and of the manipulation of the silver leaf during the gilt leather making. The aim is to study the degradation of the silver leaf and the rate of tarnishing processes, as a function of the above mentioned

45 A strip of gilt leather that has been protected from light and has an unbleached oil-resin varnish ('gold varnish'). In the brown parts the silver leaf has corroded. Detail of the gilt leather wall hanging (1740-1755, Netherlands) in Heeswijk Castle.

characteristics. In addition, the influence of restoration products on these processes will also be studied. The first results are expected in 2017. It is expected that the silver tarnishing processes can be related to the quality of the silver leaf (composition and thickness), which largely depends on the silver leaf manufacturer, as well as the manipulation of the silver during the manufacturing of the gilt leather (burnishing influences surface roughness).

Oil-resin varnish and oil paints

The coloured oil-resin varnish that covers the silver leaves to create a shiny golden surface generally consists of an heat-bodied linseed oil with lead components (from pigments such as massicot and minium), to increase drying properties, organic colourants (e.g. aloe, asphalt, saffron, dragons blood, etc.) and different tree (e.g. sandarac, colophony) or fossil (e.g. amber) resins (Schulze 2011). Drying of the varnish film occurs, under the influence of light and oxygen, through oxidative cross-linking of the oil (Phenix and Townsend 2012). The auto-oxidation process of drying oils is very slow. To speed up the drying process, in order to produce glossy films, gilt leather makers would boil the oils with lead or other metal drying agents (Schulze 2011).

Hardly anything has been published specifically on the degradation of these coloured oil-resin varnishes on gilt leather. The most frequently observed damage is caused by UV from daylight: a "bleaching" of the varnish and its colouring components (figure 45). Embrittlement, micro-cracking, and increased porosity of the oil-resin varnish has been observed and related to silver tarnishing of the underlying silver leaf by hydrogen sulphide in the ambient air (Schulze 2011).

Similar oil-resin varnishes have been used on a regular basis on easel paintings as well, as is known from technical documents and treatises from the middle-ages to the sixteenth century (Phenix and Townsend 2012). Most probably in paintings, oil-resin varnishes were applied selectively on certain pigments, depending on the colour and gloss that was desired, taking into account the colour change inherent to these varnishes. However most of these original varnishes have been lost due to past restorations. Therefore degradation studies have hardly been possible.

The coloured oil-resin varnish is quite specific to gilt leather, but has also been used as a coating for wooden objects, such as furniture and musical instruments. However little of these coloured coatings of the 17th and 18th century have survived. Often they have been removed or covered by new varnish layers. On gilt leather the coloured oil-resin varnish usually is still present. Even though they are often degraded by natural ageing, or damaged by past conservation treatments, analyses will result in interesting new information that might be extrapolated to the field of easel and panel painting.

For the painted decorations applied on top of the gold varnish of gilt leather, different oil paints and glazes have been used. Pigments mentioned in historic sources, and also analysed on historical gilt leathers, are those that were commonly used in panel and easel painting as well: lead white, chalk, earth pigments, yellow and red lead and arsenic pigments, vermilion, blue and green copper containing pigments, indigo, Prussian blue (18th century) and carbon black (Schulze 2011). Organic dyes and lakes, such as cochineal and madder, have been used extensively, either as transparent glazes or mixed with lead white. Historic sources indicate that for these glazes heat-bodied oil-resin mixtures were used as a medium.

Within the realm of paintings conservation extensive research has been done into the degradation of oil paint (Van Loon et al. 2012). From the middle ages onwards traditionally linseed oil was used for painting. Linseed oil chemically consists of triglycerides bonded with esters of long chain tri- or di-unsaturated fatty acids. Drying of the paint film occurs under the influence of light and oxygen. The unsaturated fatty acids undergo a radical chain reaction, whereby oxygen atoms are incorporated to form cross-links between the different chains, resulting in a strong three dimensional network. In this drying process pigments play a crucial role. They can speed up drying (e.g. lead-white, verdigris, and smalt), or retard the drying process (e.g. carbon black, lakes). Pigments also play a crucial role in the degradation processes occurring within paint films.

Degradation of oil paint implies chemical, physical and optical changes in the artwork, which occur naturally over time, and are dependent on the composition of the paint, such as type of pigments, particle size, type of binding medium and the proportion to the pigment, the use of additives and extenders, the thickness of the paint film, and the layer build-up (Van Loon et al. 2012). Environmental conditions, such as light, moisture, heat and internally generated or atmospheric pollutants, influence ageing processes. Upon ageing various breakdown reactions occur within the polymer network, such as oxidation and hydrolysis. Breakdown products from hydrolyses (carboxylic acid groups) can be stabilized by interaction with certain metal cations from pigments (or driers). Other breakdown products (free-fatty acids) may react with lead-, zinc-, or copper containing pigments to form the so-called metal soaps. These compounds, together with other unbound reaction products, can move or diffuse through the paint film and can even be extracted by warmth or solvents.

The chemical processes underlying the degradation of paint have been extensively studied. These can be divided into the drying and ageing of the binding medium, pigment-medium interactions (both briefly described above), pigment alterations and surface changes such as efflorescence, fatty deposits and crust formations (Van Loon et al. 2012). Within the scope of this white paper it is not possible to discuss all of these. Most of the pigment degradations described in

literature can be encountered on gilt leathers as well, but may not have been reported specifically. Examples are the photo-chemical degradation of organic red lakes (e.g. madder, cochineal) and blue indigo (fading) (Ioele 2011), and light induced degradation of yellow orpiment (increased transparency, or browning and darkening). Examples of pigment-binder interactions are the degradation of green copper resinate (turning brown or even black). Other degradations observed, and related to pigment-binder interactions, are typical wrinkling pattern of medium rich paints, due to the high absorption of oil by certain pigments, as can be seen in the dark red paint on the gilt leather of Heeswijk Castle.

Crack-patterns typical for the paint layer build-up of gilt leather have been reported (Moroz 1995, Schulze 2011). Certain paints may be cracked into large islands, resulting from a difference in drying properties of the oil-resin varnish and the overlaying oil paint. The upper paint layer dries faster than the underlying oil-resin varnish. Cracks in the oil paints can also be a result of local heating by direct sunlight in the early years of the gilt leather, when the oil-resin varnish has a far greater plasticity than the oil paints. When heated it softens whereas the oil paint does not, and cracks as a result. The entire variety of crack patterns that are seen on gilt leather are not as well understood as those on paintings and identification of the different patterns is desirable.

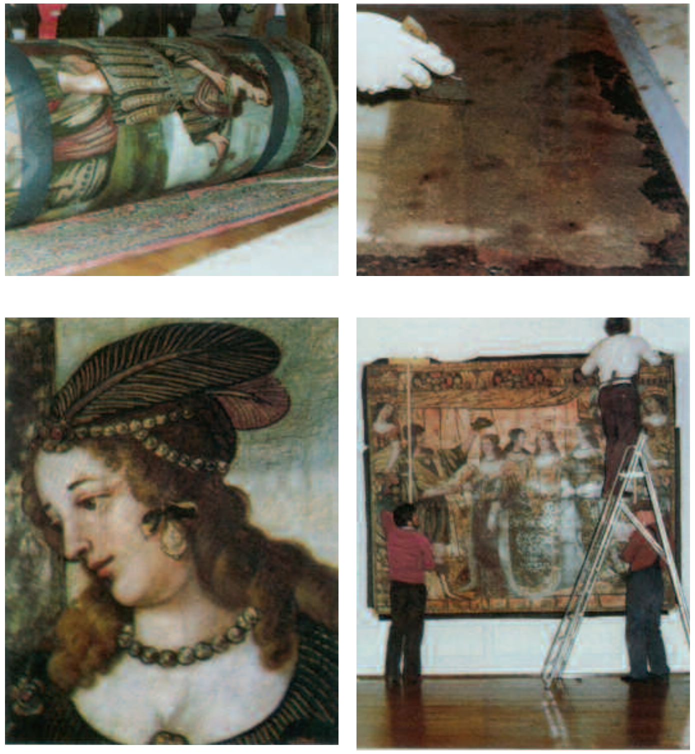
As a result of the constant 'moving' of the leather in reaction to changing RH levels, the oil-resin vanish and the paint layers crack into various patterns, depending on the composition of the paints. Moroz has been studying and classifying crack patterns on gilt leather (Moroz 1995). He found crack-patterns on gilt leathers that corresponded with the patterning of the blood vessels of a calf skin.

Next to the degradations that result from 'natural' ageing, some other severe degradations of the glazes and paints have been caused by past restorations, and are very specific to gilt leathers. Treatments, such as cleaning, oiling or re-varnishing, performed in the 18th, 19th or 20th century may have a tremendous effect on the 'sensitive' oil-resin varnish, and the overlaying oil paints. This will be described in the next section.

EFFECTS OF PREVIOUS CONSERVATION TREATMENTS AND MATERIALS

The use of oil dressings and emulsions in leather conservation

The use of oils to lubricate, soften, strengthen or protect leather originates in leather manufacture. After tanning, oils or fats would be introduced to prevent the leather fibres from sticking to each other, and to make them flexible and soft (Kite 2006). These positive effects were believed to apply to aged leather as well. As a result oiling has become common use in leather maintenance and conservation, during the second half of the 20th century (Lem 2011). The main constituent of lubricants used in leather conservation was a vegetable or animal oil of saturated fatty acids (non-drying



46 The conservation of the gilt leather wall hanging (1650-1700, Southern Netherlands) in Dunster Castle (UK) in the 1980's. At the time it was considered best practice to apply fat or oil as a lubricant to leather and gilt leather. A dressing of 6% fat content was applied to the back side.

oils), which were either dissolved in a solvent (oil dressing) or emulsified in water by means of a surfactant (oil emulsion).

In the past the maintenance and conservation of gilt leather was performed by leather craftsmen. In the 20th century conservators from different backgrounds and specializations were commissioned, often leather conservators, and occasionally paintings restorers. This resulted in the application of best practices in their field (at the time) to the gilt leather objects, such as glue-paste or wax-resin linings, or the use of oil dressings or emulsions to 'feed' the leather. In the Netherlands during the second half of the 20th century most gilt leather restorations included the application of oil, in the form of dressings and emulsions, as this was considered beneficial (Posthuma de Boer 2012). Publications and conservation reports show that in practice usually a 10% oil dressing or emulsion was applied to the verso (or flesh) side of the gilt leather (Lem 2011) (figure 46). Occasionally these were also applied on the painted side of gilt leathers.

In the 1990s the negative side effects of leather dressings on historical leather, such as a decrease in flexibility and softness, were observed by book conservators (Lem 2011). Only recently the effects of oil treatments on the physical and chemical properties of leather have been examined in experimental studies (Blaschke 2008, Izdebska 2008). Even though the methodology of the experiments are still subject of debate, this research has brought to the attention some long term effects of the use of lubricating products on leather, such as gloss and colour change (darkening) and stiffening.

Degradation of over-oiled gilt leather

Degradation of gilt leather caused by past conservation treatments with oil emulsions or -dressings has been observed and examined both in the Netherlands and in Germany (Jägers 1980, Muller 1986, Göpfrich 1998, Schulze 2011). Over-oiling of gilt leather hangings in several German castles has led to a softening and partial dissolving of the varnish and the paint layers. These studies have raised the hypothesis that oils applied at the verso side of gilt leather hangings migrate through the leather to the decorative finishes (Jägers 1980). Darkening, an effect of silver tarnishing, caused by oiling has also been suggested (Kretschmar 2004, Schulze 2011). In the seventies oil emulsions were used on gilt leathers that had been chemically treated with concentrated sulphuric acid or sodium bisulphite (sulphated oils) (Posthuma de Boer 2012). Possibly the presence of these sulphur compounds have contributed to tarnishing reactions.

Degradation phenomena related to darkening of the decorative layers of gilt leather on two examples of Dutch 18th century gilt leather hangings – Sint Pietershof in Hoorn and Weeshuis der Hervormden in Schiedam – have been systematically characterized, both on a macroscopic and microscopic level (Posthuma de Boer 2012). Results indicate that degradation processes, related to the darkening, are taking place in both the silver (corrosion) and varnish layers (softening, darkening). The main components detected in

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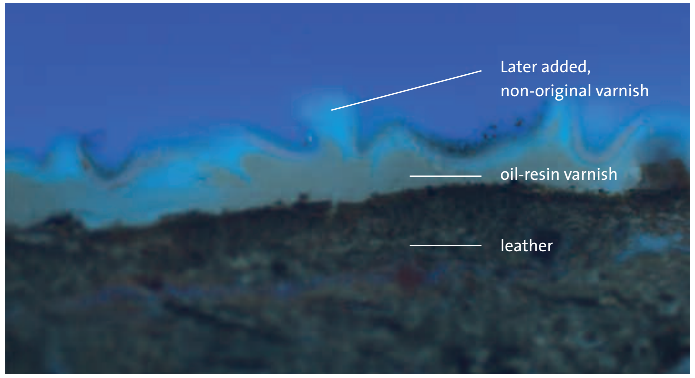

47 Detail of a severely darkened part of the gilt leather wall hanging (1783, Netherlands) in the Weeshuis der Hervormden, Schiedam.

48 Cross-section of the darkened parts of the Schiedam wall hanging showing heavily distorted varnish layers, caused by the use of non-drying oils or solvents in earlier restorations (UV-fluorescence microscopy 200x).

the varnish can be traced back to leather conservation products (oil dressings or emulsions) used in the 1970's and 1980's, suggesting a migration of these products into the varnish layer. Observations of these severe damages to decorative layers has led to a strong discouragement amongst experienced gilt leather conservators of the use of any leather maintenance products on gilt leathers.

Past restoration treatments of decorative surfaces

Most gilt leathers show traces of surface cleaning, such as abrasion, re-varnishing or the application of other protective coatings. On almost all gilt leathers that have been conserved in the Netherlands recently – e.g. Sint Pietershof Hoorn, Weeshuis der Hervormden of Schiedam, town hall Maastricht, town hall Venlo, Heeswijk Castle – later added varnishes have been observed, a phenomenon also perceived abroad (figures 49-51). During recent analyses and treatment of the gilt leather of the Maastricht town hall, SRAL has noticed that the original coloured oil-resin varnish has dissolved (figure 61) when later varnishes where applied (using of solvents). It seems that the oil-resin varnish is migrating into the upper (newer) coatings. This effect has also been observed in the surface layers of the gilt leather in the Weeshuis of Schiedam (Posthuma de Boer 2012) (figures 47, 48). The migration of the oil-resin varnish may also have been caused by diffusion of non-drying oils which were applied to the leather during past restorations. This is a serious risk for the preservation of gilt leather in general, but specifically for planned restoration interventions, such as surface cleaning and varnish removal. This effect needs further investigation.

CLIMATIC CONDITIONS AND DEGRADATION

Relative humidity

Leather is a hygroscopic material that absorbs and desorbs water in relation to the relative humidity (RH) of the surrounding air. Its flexibility depends to a large extend on the amount of water that it has bound in its fibres. Over time, however leather loses much of its bound water by hysteresis (Florian 2006). Continuous RH cycling causes a gradual dehydration of the leather fibres, which shows as a loss of flexibility, an increase in brittleness and shrinkage. A low RH may cause mechanical damage, such as tears. A high RH may lead to deformations, and may create tension in the decorative layers, leading to delamination. Very high RH-values (>70%) increase the chance of mould growth.

The ENVIRONMENT leather project pointed out that sudden changes in RH are a high risk for leather (Larsen 1996). Due to degradation processes, such as oxidation and hydrolysis, fibres depolymerize and the structure of the leather becomes less compact. As a result the rate of absorption and desorption processes in the fibres increases, and in addition also the amount of moisture sorption increases. The rate of sorption processes is directly related to the degree of internal heat produced (heat of condensation), which causes mechanical damage to the fibres. As the speed of

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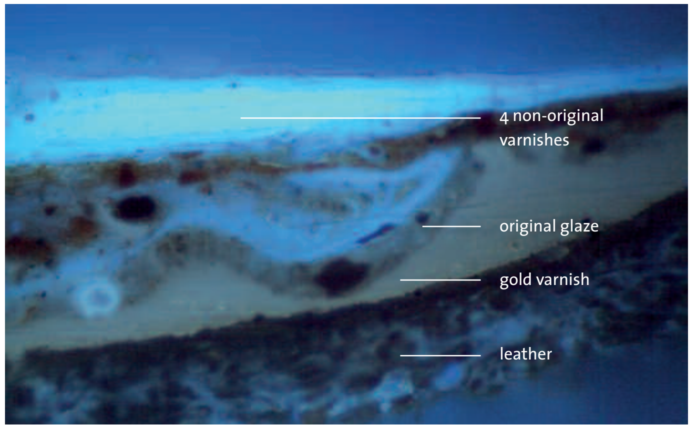

49 One of the panels of a large Venetian gilt leather wall hanging (1656) with old testament scenes, painted by Jacques Courtois, known as Giacomo Borgognone, Grand Staircase at Knowsley Hall (UK).
50 Detail showing the darkened surface due to later non-original varnish layers.

51 Cross-section showing 4 different later added varnishes, separated by thin dark lines (dirt), on top of the original gold varnish and glazes from 1656 (UV-fluorescence microscopy 500x).

sorption processes tend to increase upon ageing, the mechanical stresses increase proportionally. For leather in archives and museum collections it is advised to keep the RH as constant as possible. In the case of gilt leather hangings in situ maintaining a constant RH is often not realistic. Gradual seasonal changes are usually no problem for the conservation of gilt leather. Sudden changes may be avoided by using humidity buffering materials behind the wall hangings.

High relative humidity, and humidity cycling, is a risk for the decorative layers. It may cause stress between the different layers and delamination, induces corrosion processes in the silver leaf, and cracking of paint.

Temperature

For leather materials one can follow the rule of thumb that an increase of temperature (T) by 5°C will halve the lifetime of the object (Michalski 2015). Schulze compared the shrinkage temperature (TS) – an indicator for the condition of leather – of gilt leather wall hangings in heated and unheated rooms in Moritzburg Castle (Germany). He observed a considerably lower TS for the leathers in heated rooms, meaning a decrease in condition of these wall hangings. He concluded that temperature is of as much importance as relative humidity for the conservation of gilt leather.

Temperature gradients may also cause large unwanted RH differences, causing cracking or delamination of the decorative layers (Mecklenburg 2007). Recent research on painted canvas wall hangings in situ (Hofkeshuis, Almelo) points to a relation between temperature gradients and increased degradation of lead white oil paint (Keune et al. 2016).

Light, ultraviolet and infrared

Light remains an important agent in deterioration, as a lot of wall hangings are located in places without any light protection measures. The UV-range of the spectrum causes damage mostly to the paint and varnish layers. Colour changes have been observed in the oil-resin varnish, as well as certain (organic) pigments. Cracking of the paints and varnishes is a second sign of deterioration (Michalski 2015). Direct sunlight (infrared range of the spectrum) can cause a high increase in temperature locally. These temperature gradients cause local changes in relative humidity, which have an effect on both the leather and the decorative finishes. The leather will show deformations as a result of RH differences. Changes in RH and temperature may cause mechanical as well as chemical damage, as described above.

Pollutants

Atmospheric pollutants, such as ozone, sulphur dioxide, nitrogen dioxide and carbon dioxide, play a significant role in the degradation of leather (Florian 2006). Most research has been done on degradation mechanisms involving sulphur dioxide. Under the influence of sunlight sulphur dioxide will convert to sulphur trioxide, which may react with water to produce sulphuric acid which is damaging to

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leather. Sulphur trioxide under the influence of oxygen may form ozone, a strong oxidizing agent.

Hydrogen sulphide plays an important role in the corrosion of silver. It is a gas that is formed when biological materials break down under the absence of oxygen.

CONCLUSIONS

Knowledge on degradation processes and agents of deterioration is available for each of the materials in gilt leather – leather, silver, pigments, paints and varnishes. However very little research has been done on the chemical and physical interactions between the components of the different materials and their degradation products. The most important degradation phenomena have been described, on a macro- as well as on a micro level, such as silver corrosion, and the darkening, softening or embrittlement of the varnish and paint layers. The degradation processes underlying these phenomena are not well understood yet. The influence of external factors, such as climatic conditions, has not been studied either.

Illustrated glossary of condition (or degradation)

From a conservation perspective there is a need for an overview of degradation phenomena on a macro-level. An illustrated glossary should make conservators of different disciplines, curators, restoration architects and owners aware of material degradations and changes over time. Together with preventive conservation guidelines this can be a first step in improving conservation conditions for these heritage artefacts.

Leather

Mechanisms underlying leather degradation have been studied extensively during the STEP and ENVIRONMENT leather projects during the 1990's. These studies included the identification and quantification of degradation products. The effects of environmental conditions have also been examined. Tannage is very significant in understanding deterioration. Tannages of a hydrolysable type are known to be more resistant to degradation than those of a condensed type. Selecting analytical techniques to identify actual tannages would be desirable. Environmental conditions are very important agents of deterioration for leather. Studies on the impact of the environment on the conservation of gilt leather is scarce and should be conducted.

Silver leaf

Silver corrosion has an enormous impact on the visual appearance and hence our perception of these cultural artefacts. The CORD' ARGENT project focuses on the relationship between the material composition and the manufacturing processes of the silver leaf and corrosion processes. The effect of previous restoration treatments will be taken into account as well. First results are expected in 2017. Future research should identify corrosion products and processes, resulting in the identification of possible causes. Degradation of the other materials in gilt leather may play a crucial role and should be studied, such as increased porosity of the adhesive layer under the silver foil, and the overlaying oil-resin varnish. Other material factors influencing corrosion need to be investigated as well, such as acidic tannins in the leather or sulphur or copper containing pigments, such as orpiment, vermilion, verdigris or copper resinate. Migration of silver degradation products into leather, glue or varnish layers has been suggested, but should be verified by research. Influences such as past conservation treatments with (sulphated) non-drying oils or environmental influences such as atmospheric gaseous pollutants, moist and high levels of relative humidity, and UV-radiation also need further research.

Gold varnish, glazes and paints

Degradation of the paint and varnish layers also has a high visual impact. 'Natural' degradation processes of pigments and binding media by temperature gradients, moisture and light is a continuous field of study within the conservation of paintings. However the effect of past conservation treatments specific to gilt leathers, such as the use of various oil products, on pigments and the different binding media is a topic that needs more investigation. The effect of past solvent treatments, including re-varnishing, specifically on the oil-resin varnish needs to be studied further as well. This last topic is of high importance to the development of improved conservation treatments, as is the effect of solubilisation and migration of original gold lacquers (varnishes) by later applied varnishes.

RECOMMENDATIONS FOR NICAS

Learning from conservation history

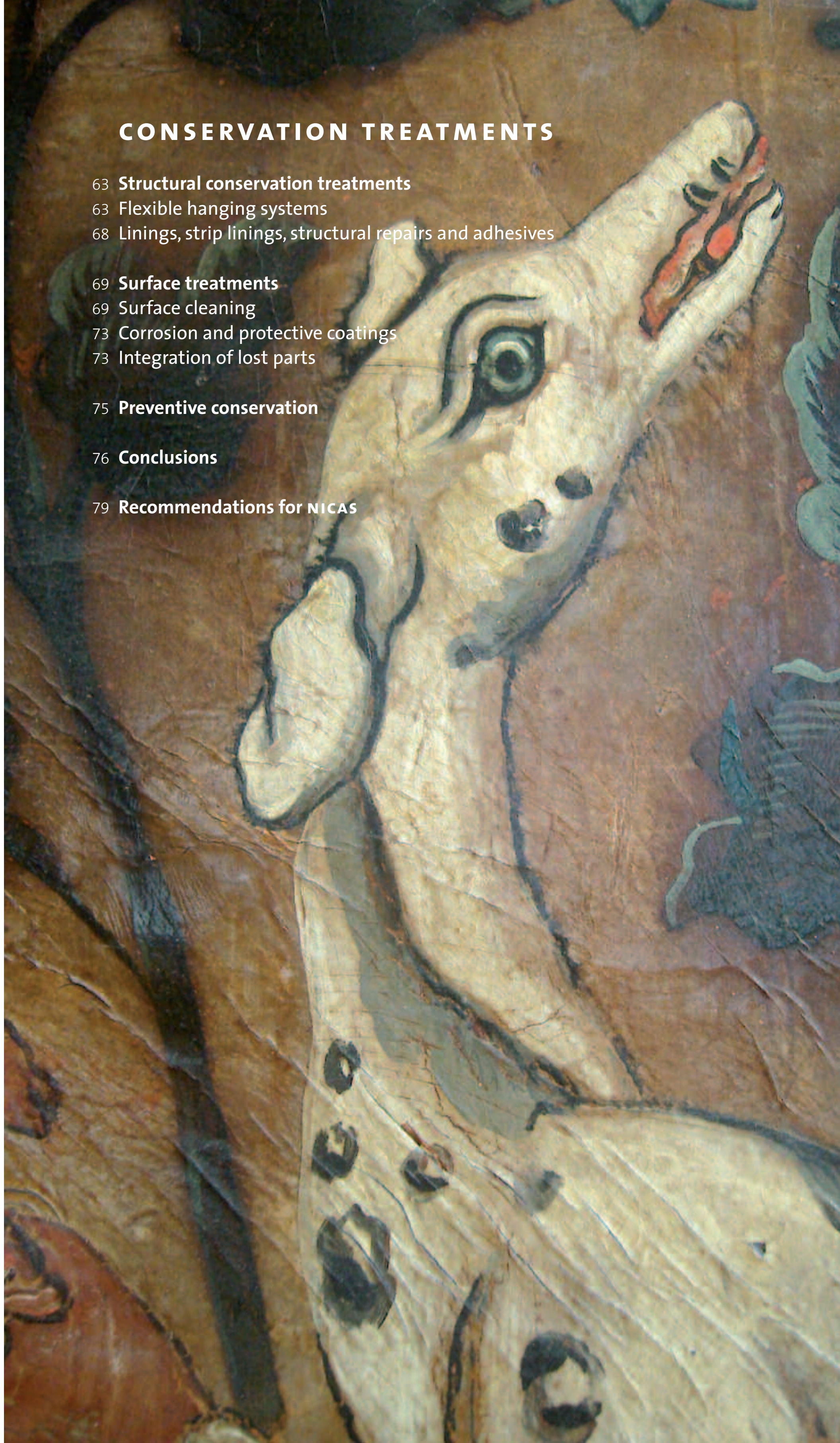
The study of the effects of past conservation treatments on historic objects was considered a way to start investigating degradation mechanisms. As artificial ageing of leather has shown that it is very difficult to get results that are representative for natural ageing, model studies may not be sufficient. Especially in the Netherlands there is a large amount of data available about conservation treatments of gilt leathers in the past 30- 50 years, mainly at the Cultural Heritage Agency (RCE), but also at the Rijksmuseum. The objects that have been treated are available for study, and their condition should be studied in detail (for example the Rijksmuseum gilt leather collection and the former restoration studio of Henk van Soest). The topic of leather oiling and the effects on silver, varnish and paint layers, could lead to an in-depth study of silver corrosion and related degradation mechanisms. Within NICAS the collaboration with corrosion experts offers great opportunities. The experimental (technical) possibilities will be discussed further in the diagnostics chapter.

Study and analyses of best preserved objects and their environments

A topic of great importance is the relation between environmental parameters (RH, temperature, pollutants) and the condition of gilt leathers. For degradation studies there is a need to find examples that have a known history of environmental conditions to which they have been exposed to. It would be interesting to study leathers of the same decorative scheme, kept under the same environmental conditions, that have differences in degree of degradation. Research of indigenous gilt leather panelled rooms (e.g. Skokloster, Moritzburg) could establish the factors accounting for differences in condition.

Additionally research should be carried out on objects that are best preserved through the ages. Good examples of gilt leathers preserved in their environment should be identified (for example Skokloster castle, or the Portuguese synagogue as best cases).

Why are certain gilt leathers so well preserved, and others not? Is it because of the differences in quality of the materials themselves, or because of different environments, or because of different conservation histories? As has already been suggested in the previous chapter on technical art history, the analyses of silvered leathers that have not oxidized will help to understand the material and environmental circumstances needed for preservation, and could aid to develop preventive conservation measures.



CONSERVATION TREATMENTS

52 A Lycra® strip lining for a flexible mounting system for one of the gilt leather wall hangings in the Frans Hals Museum, Haarlem.
53 The flexible hanging system with Lycra® installed in 1974 by Henk van Soest, Sint Pietershof Hoorn.
54 The removal of the Lycra® strip lining of the Sint Pietershof wall hangings in 2011 by SRAL, before installation of a new flexible mounting system.

Gilt leather is a complex material that requires an interdisciplinary approach in conservation. In the past however, craft-led conservation practices focused solely on either the leather support, and rarely on the decorative surface layers. As a result conservation treatments have been performed that are inapt, and damaging to one or more of the materials in gilt leather. In the previous chapter some examples have been described, such as starch paste linings (from paintings conservation), and the use of leather dressings (leather conservation).

The problems that conservators face today are not only the result of past restorations, but also of the fragility (ageing) of the materials itself and sometimes the result of inappropriate climates, or micro-climates. But most of the times the effects of a combination of all of these factors are encountered. The most urgent and important conservation challenges today are hanging systems that are degrading, inappropriate linings, the darkening of later added varnishes, the effect of non-drying oil products (leather dressings and emulsions) into the decorative layers, the damage of gold lacquers by later solvent varnishing, the corrosion of the silver leaf, and unfavourable climatic conditions.

Most important conservation issues are taking place both on a structural level, as well as on an esthetical level. This chapter gives an overview of the current state of the art in conservation practices.

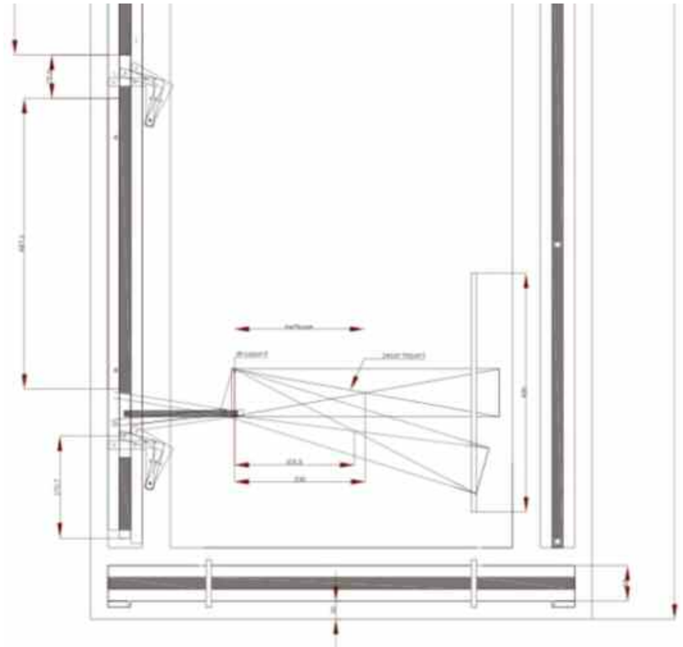
STRUCTURAL CONSERVATION TREATMENTS

Flexible hanging systems

One of the major issues in the conservation of gilt leathers is the design of flexible tensioning systems. Most of the gilt leather wall hangings are preserved in situ in historical buildings, sometimes in their original location, sometimes moved to a new 'home'. Most of these places, such as palaces, castles, town halls, etc., have a public or a museum function, but are not able to meet strict museum climate standards. Temperature and relative humidity in these places is not constant, but fluctuates in reaction to the outdoor climate, indoor heating, the amount of visitors, etc. Damage to the leather especially occurs, as a result of the malfunctioning of the introduced climate systems or central heating, causing large fluctuations in temperature and RH.

As a consequence of the hygroscopic behaviour of leather fibres, gilt leathers that have been fixed to the wall, or to wooden battens, show severe mechanical damage, such as deformations and tears. From the second half of the twentieth century flexible hanging systems have been designed that allow movement of the leather, and prevent mechanical damage. Various types of systems have been designed, which can be grouped according to the way tension is applied to the leather: flexible textiles, springs, weights (gravity), or hanging loose (no tension) (Posthuma de Boer 2015).

In the Netherlands flexible hanging systems were introduced in the 1960's by the late gilt leather conservator Henk van Soest. He used the elastic textile Lycra®, an elastomer consisting of



55 The construction drawing for a flexible hanging system using weights. Design by Elizabet Nijhoff Asser and Godfried Brands, 2013.

56 A wooden panel with integrated flexible mounting system, for one of the gilt leather panels of Heeswijk Castle. Design by Godfried Brands, 2013.

polyurethane, to hang and tension gilt leather wall hangings (figures 52-54). This seemed an ideal solution for the dimensional changes. Tension can be built up evenly across all sides of the panel, allowing the leather to move in all directions. It was easy to install, and when needed it could be removed (calamities). Unfortunately the elastic textile has a limited life span. Within 30 years certain polymer components degrade and leach out the material. The loss in elasticity causes the large gilt leather panels to bulge. In the Netherlands approximately 23 gilt leather wall hangings have been hung with Lycra®, and the majority of them is now in need of a new hanging system.

In the 1990's both the conservators of the Istituto Superiore per la Conservazione ed il Restauro (ISCR) (Nimmo et al. 1996 and 1999) and Schulze (Schulze 2004) introduced more durable flexible hanging systems using rolling aluminium tubes and coil springs. For these systems a strip lining is adhered to the sides of the gilt leather and connected to the springs. SRAL introduced a simple system of a series of small extension springs which connected the strip lining directly to the wall (Van Kempen and Koldeweij 2005). To determine the desired spring constant one needs to know the expected dimensional change and the yield strength of gilt leather. The use of springs introduces its own limitations to the system, because the amount of tension increases linearly with the change in dimension. The elastic system of ISCR is adjusted as a function of an imposed preload, and as a result tensions induced by hygrometric variations can be reduced accordingly.

Nijhoff Asser has developed a flexible tensioning system based on the use of weights (Nijhoff Asser et al. 2014) (a prototype in figures 55, 56). This has the advantage over the use of springs that the tension is constant, evenly distributed, and precisely determined in advance. A last solution for the hanging of gilt leather is to only fix it from the upper side and let it hang loose on the other sides. The advantage is that the leather can really move in all directions. This option is generally chosen when it is known that the wall hanging was originally not fixed or tensioned. This can also be a desirable solution when there is minimal available space behind the leather to place a frame or tensioning system.

As has been described above when designing a tensioning system for historical gilt leather hangings one needs to take into account several variables connected to the properties of the material itself, such as the tensile strength, and the sorption behaviour (expected shrinkage and expanding) of the leather. But also contextual variables, such as RH fluctuations in the ambient air, which will determine shrinkage and expansion of the leather fibres.

The mechanical properties of gilt leather have been studied by a collaboration of ISCR with the Department of Mechanical and Aerospace Engineering of the Sapienza University of Rome (DIMA) (Nimmo et al. 1996), as well as by Nijhoff Asser (Nijhoff Asser et al. 2014). DIMA performed tensile and yield strength tests on historical gilt leather samples that had undergone different

CONSERVATION TREATMENTS

57 The climate and displacement monitoring system, designed and installed by Elizabet Nijhoff Asser for one of the gilt leather wall hangings at manor house of De Wiersse, Vorden in 2015.

58 The structural repairs of one of the gilt leather wall hangings of manor house of De Wiersse, Vorden in 2014, in the RNA studio.

degrees of tooling (punch marks). The samples were tested in the different fibre directions. Results showed that the tensile strength of historical gilt leather varies a lot (4 – 7.5 MPa, 4-20%) depending on the orientation of the fibres in the leather, the state of conservation and the degree of tooling. Nijhoff Asser performed some very simple tensile strength tests on random 18th century gilt leather fragments (leftovers from earlier refurbishing). She came to a similar range of results: 3.2 – 8 MPa (breaking load). However to establish safety margins for tensioning historical gilt leather wall hangings, additional testing should be done following the standard test methods for leather [The American Society for Testing and Materials (ASTM) has standard test methods for measuring elongation (ASTM D2211) and tensile strength of leather (ASTM D2209), as well as several specific tear strength tests]. Correlating the strength to the condition of the leather fibres would be most helpful.

The sorption behaviour of historical gilt leather has been experimentally determined in the context of conservation projects. Schulze had measured a mass difference of 0,6% on a historical gilt leather, as a result of a 40% RH difference (Schulze 2004). The mechanical behaviour of gilt leather related to temperature and RH has also been examined in the study performed by ISCR and DIMA. On the basis of the collected data the coefficients of hygrometric dilation were calculated. The parameters were of the same magnitude as those calculated by Schulze, and have been used for the design of controlled tensioning systems. Nijhoff Asser measured 0,5% mass change on a 40 year old restoration leather (40% RH difference) (Nijhoff Asser et al. 2014). Julian and Stappers have measured the hygroscopic sorption curves for historical gilt leather, indicating the relationship between the equilibrium moisture content in the leather and the RH of the ambient air at constant temperature. Response time testing was also done for gilt leather samples, indicating the rate of moisture absorption and desorption. These tests were done in relation to a project on the influence of backing materials on the microclimates surrounding gilt leather wall hangings. The results have not been published (Julian and Stappers 2014).

Nijhoff Asser is currently monitoring the hygroscopic behaviour of tensioned gilt leather in response to climatic conditions at manor house of De Wiersse, Vorden. A time lapse camera is recording the movement of the gilt leather attached to a flexible tensioning system. Vertical and horizontal displacements are measured, which can be correlated to relative humidity measurements. It is a simple and effective tool to monitor the behaviour of the gilt leather, and to check the functioning of the tensioning system. Furthermore it has proved to be very instructive in showing the impact of the climate visually (figure 57).

In 2016 a collaborative research project of ISCR and DIMA starts on the verification of elastic tensioning structures for paintings on canvas, in which gilt leather hangings will be included. Within this context the development of non-invasive and remotely operated sensor devices for the measurements of physical parameters (T, RH and deformation) will be addressed.

Different flexible hanging systems have been designed over the course of 20 years. Some research has been done into the mechanical properties of gilt leather, as well as the structural behaviour and response to climatic conditions. However for the further development of flexible hangings which are safe and allow for optimum movement of the large gilt leather panels, more research is needed. It would also be useful to evaluate the tensioning systems that have been installed the past 10-20 years on their functioning. Of special interest is to investigate whether the top part of large gilt leather panels has been stretched, as it bears most of the load.

Linings, strip linings, structural repairs and adhesives

The seams between the different leather panels are structurally the weaker parts within a gilt leather panel. Repeated re-sewing during maintenance or restoration treatments may have created multiple perforations and weakened the leather. These have sometimes been supported by adhering a new strip of leather (figure 58) or other materials, like linen or woven polyesters. The seam may also have been cut off altogether and replaced by new materials. In some cases the back of the gilt leather may have been lined all over with a backing material of various natural or synthetic cloths. Case-studies on gilt leather restorations describe the encountered earlier structural treatments, such as traditional glue-paste linings with linen or cotton cloths, but also 20th century linings with polyvinyl acetate adhesives and polyester cloths. In recent projects a variety of natural or synthetic materials have been used for strip linings, amongst others polyester cloth with BEVA® 371 (Nijhoff Asser et al. 2014), or linen cloth (Van Kempen and Koldeweij 2005) or vegetable tanned leather with parchment glue (Schulze 2004). Lining a gilt leather in its entirety is very invasive and is rarely performed nowadays.

Adhesives and backing materials have been extensively tested within the context of textile and leather objects conservation (Dignard 2013). Iafrate et al. have performed a comparative study on adhesives (wheat starch paste, methyl hydroxyethyl cellulose, ethylene vinyl acetate and acrylic co-polymers) and support materials (Japanese paper, non-woven nylon fabric, and alum tawed calf leather) for the specific use in structural repairs of a large gilt leather panel that would be tensioned (Iafrate et al. 2011). Not only the mechanical properties of the separate materials were obtained, but also the properties of the joints between these materials were analysed. Similar types of studies could be useful for the assessment of (strip) lining materials and adhesives. Furthermore a risk analyses of certain types of adhesives (using heat, solvent or moisture) would be of benefit for current conservation practices. This could result in a set of requirements that could be used for the development of adhesives suitable for use in gilt leather conservation. An alternative to BEVA® 371 for example would be highly desirable.

Within the conservation of leather book bindings a lot of research has been performed into the development and testing of high quality and sustainable conservation grade leather. Todays industrialized leather industries produce mostly chrome-tanned leather with chemical and mechanical properties that are incompatible with historical vegetable tanned leathers. The production process of vegetable tanned leather for conservation purposes still differs much from historical tanning practices, resulting in different quality leathers. Schulze has set up a project with the Forschungsinstitutes für Leder und Kunststoffbahnen (FILK) in Freiberg to develop tanning processes that resemble as much as possible traditional practices (Schulze 2011). The aim was to produce conservation leather with chemical and mechanical properties and sustainability similar to historical gilt leather in order to avoid any unwanted differences in tension.

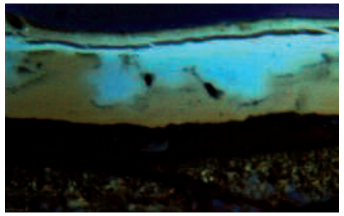
SURFACE TREATMENTS

The decorative layers of gilt leathers have received little attention, compared to the work that has been done on a structural level. In the conservation of gilt leather wall hangings, usually a restrictive approach is chosen regarding the surface layers, characterized by minor conservation interventions. Such an approach is partly due to limited budgets, the priority is given to structural issues, and partly due to the lack of knowledge on the effects of surface treatments on the complex material composite layering of gilt leather.

Conservation problems regarding the painted decorative finishes of gilt leather overlap to a great extend with those encountered in the conservation of paintings, such as cracking in the paint and varnish layers, delamination or paint loss, degradation phenomena of specific pigments, or obscuring and darkening of later added varnishes. Little has been published on surface treatments within the literature on gilt leather. Within the realm of paintings conservation, significant advances have been made in the development of surface cleaning techniques, some of which could be of interest to gilt leather. These techniques deserve to be explored, as they would improve the aesthetic perception, and thus the appreciation of gilt leathers, to a large extend. The applicability of these techniques however, needs to be carefully assessed, taking into consideration the specific varnish and paint layering of gilt leather, the vulnerability of the silver leaf, as well as the porosity of the support.

Surface cleaning

Gilt leathers over the course of time have often been covered with an additional natural resin varnish during restoration treatments. Quite a few examples of gilt leather wall hangings have a yellowed, or obscured surface. Varnish removal could considerably improve the 'readability' and 'perception' of the wall hangings, especially in the case of the ones with painted scenes. When selecting solvents and application methods for the removal of later added varnish special attention should be paid not to cause any damage to the original



59 Two of the smaller panels of the gilt leather wall hangings (1739, England) from the Mayor's room of the town hall in Maastricht, left panel before conservation, right panel after conservation.

60 Detail of one of the wall panels, before conservation, showing amongst others the darkening of the green paint (containing orpiment) and the silver leaf around it.

61 A cross-section showing heavily distorted varnish layers, caused either by the use of non-drying oils or by the use of solvents during earlier restorations (uv-fluorescence microscopy).

glazes and oil-resin varnishes. Prior to any conservation intervention extensive examination of the composition and paint layering should be performed. As has been described in previous chapters specific parts of the painted decoration may still be covered with original varnishes for glossy effects.

Technically, partial varnish removal is a challenge and should only be considered after extensive testing. Both the coloured oil-resin varnish, and coloured glazes should be considered 'solvent-sensitive' paints, because of their small pigment to binder ratio (medium rich), and the addition of non-polymerizable components (natural resins) (Phenix and Wolbers 2012). These 'solvent-sensitive' paints have an increased risk of swelling, softening and leaching [the extraction of low molecular weight components, resulting in brittleness of the paint film]. As has been described in the previous chapter, oil-resin vanishes may have become brittle and mini-cracks may have formed, exposing the underlying silver leaf. The silver leaf in its turn may be cracked, giving access to the even more porous leather substrate. Extreme care should be taken with solvent cleaning. As has been described in the previous chapter as well, previous conservation treatments with solvents may have disturbed the varnish and paint layering to a large extend, complicating planned surface treatments even further (figures 59-61).

SRAL has made important advances in controlled solvent use for varnish removal on paintings by developing a 'tissue-gel composite cleaning technique' (Fife et al. 2011). Thickened solvents (organic solvents gelled with cellulose ethers) are applied to the painted surface with a tissue, and held in place for a short period of time. A second dry absorbing tissue is subsequently placed above, which is manipulated to further absorb the dissolved non-original materials (figures 62-64). One of the advantages of this technique is that it restricts both solvents and dissolved products moving through the painting structure to the reverse side. The technique has been applied successfully for the removal of a non-original varnish on the gilt leather of the town hall in Venlo, during a conservation treatment by SRAL.

The challenges of partial varnish removal in paintings conservation are also addressed within *Iperion*, a platform for the European research infrastructure on cultural heritage. It is a collaboration of several research institutes and offers advanced diagnostic tools for research on cultural heritage. Within this large research project specific conservation challenges are addressed as well. One of the topics is the development of diagnostic strategies for assessing the cleaning of paintings. Outcomes of this project could potentially be interesting to gilt leather conservation as well.

62 Pilot conservation of the gilt leather wall panels (1734, workshop of Carolus Jacobs, Mechelen) of the board room in the town hall of Venlo by SRAL in 2015. A later added varnish was removed by using the 'tissue-gel composite cleaning technique'.
63 Two of the gilt leather panels from Venlo before restoration. Pigment analyses assessed strongly discoloured surface layers.
64 The gilt leather panels from Venlo after restoration. The controlled removal of the darkened varnish layers revealed the original green background.

Corrosion and protective coatings

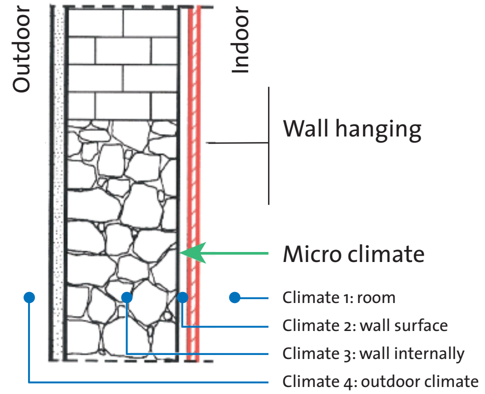
Other degradation phenomena, very specific to the layer build up of gilt leather, for example corrosion of the silver leaf, may benefit from new conservation strategies. As silver corrosion seems to relate to the porosity of the overlaying oil resin varnish, one could tend towards solutions of protective coatings. However the corrosion processes, but also the properties of the protective coatings (both the glue and varnish layers on either side of the silver leaf), need to be much better understood before any conservation solution can be developed. In the previous chapter it was described that the manufacturing processes of both silver leaf and the leather are of influence on the development of corrosion. For example the percentage of trace elements in the silver and the thickness of the silver leaf may play a role (Radepont et al. 2015). Schulze found that unbound tanning agents or other substances in the leather also trigger corrosion processes of the silver leaf (Schulze 2011).

Electro-chemistry offers solutions for the cleaning of tarnished silver objects. Successful tarnish removal has been performed with an electrolytic cleaning pencil (Pleco) on a silver plated reliquary statue of St. Maurice Abbey in Switzerland (Degrigny et al. 2015). The cleaning tool has been developed by the Conservation Research Unit at the University of Applied Sciences and Arts of Western Switzerland Arc (URARCCR). Tests have been performed with this technique on test samples of tarnished silver leaf adhered to leather, as well as on historic gilt leather fragments, mostly on parts where the oil-resin varnish coating had disappeared. The main challenge of this technique is the contact with the electrolytic solution, and the clearance of it afterwards. Contact with aqueous solutions poses the risk of delamination of the silver leaf and of affecting the degraded leather underneath. This technique may only be suitable for parts of the gilt leather where the gold varnish has disappeared or has been removed in the past.

Integration of lost parts

In many cases, parts of the gilt leather wall hangings have been lost, so the remaining gilt leather needs to be completed with inserts. For this, different strategies have been developed, using different kinds of materials. Schulze has been making reconstructions of gilt leather based on the study of historical literary sources, using materials and techniques similar to the ones that were used in the 17th and 18th centuries. Nijhoff Asser applied embossed and digitally printed Japanese paper on new leather for the gilt leather hangings of Huis Six in Amsterdam. SRAL has been using digital printing and paper moulds to mimic the surface of gilt leather. Other contemporary techniques such as 3D-scanning and printing could be interesting to explore. However for all of these options one needs to assess chemical stability and physical compatibility of the material with the historical gilt leather, avoiding tension caused by strain differences resulting from climate fluctuations.

CONSERVATION TREATMENTS



65 Schematic cross-section of a wall with a wall hanging, showing the different microclimates in the vicinity of the wall hanging.
66 Wall protection of carton coated polystyrene covered with pine wooden battens (SRAL, 2011).
67 Wall protection of spruce battens for humidity buffering (RNA, 2013).

The condition of gilt leather wall hangings is very much affected by the location where it is preserved, which in many cases is the building fabric of historic interiors. The decorative layers protect the leather from climatic influences in the room. The leather will be influenced more by the relative humidity and temperature of the space between the wall and the hanging. In case of an interior wall the microclimate behind the hanging should not differ much from the indoor climate of the room. However in case of an external wall there can be big differences depending on the humidity level inside the wall, which in its turn is dependent on the permeability of the outer shell of the building and the outdoor climate (figure 65).

In general temperatures on outer walls are lower than indoor room temperatures, and the RH is generally higher. In early spring when temperatures suddenly increase and relative humidity is high, there is an increased risk of condensation on the wall (Graupner 2004). In winter an increased risk of condensation on the wall may occur when rooms are heated and a humidifier is placed in the room to compensate for low RH levels. The extra humidity in the air may condense on the cold outer wall (Ankersmit 2009). In summer some walls (south facing) may be heated, and very low RH levels can be recorded on the inside of outer walls (Mecklenburg 2007). Next to the risk of direct water damage caused by condensation, another risk is continuous or sudden fluctuations in the RH levels of microclimates behind gilt leather wall hangings. Continuous RH cycling imposes mechanical stresses on the leather fibres and causes material fatigue. Sudden RH changes may generate internal heating which causes damage to the fibres.

During most conservation projects a wall protection is installed behind the gilt leather wall hangings (figures 66, 67). These can be made of different materials depending on their function. Many conservators have chosen spruce or pine panelling – hygroscopic materials with a high moisture buffer value (Rode et al. 2006) – with the goal of creating microclimates with a stable RH behind the wall hangings (Schulze 2004, Nijhoff Asser 2014 et al.). However research into microclimates behind paintings in enclosed environments indicates that temperature gradients are leading for the moisture distribution in (semi-) enclosed environments, filled with absorbing (hygroscopic) materials (Ligterink and Di Pietro 2007, Padfield et al. 2001). It has been shown that temperature gradients can induce large local RH differences. Further research into microclimates behind wall hangings and the introduction of hygroscopic isolation materials is needed.

CONCLUSIONS

Interdisciplinary teamwork
The conservation and restoration of gilt leather objects and wall hangings is complex due to the sensitive nature of the combination of organic and inorganic materials. As has been pointed out in the previous chapter, material characteristics and ageing dynamics of gilt leather are partly influenced by the combination of materials. It thus requires specialized knowledge transcending conservation practices developed within individual conservation disciplines. Interdisciplinary collaborations between conservators of different disciplines are necessary, but do require the familiarity of the collaborators with the material gilt leather.

Flexible hangings systems
On a structural level specialized conservation knowledge has been developed to a large extent. Different flexible tensioning systems have been developed successfully over the past 25 years, accommodating the dimensional changes of large gilt leather panels due to relative humidity fluctuations. However more knowledge on the physical properties of aged gilt leather could contribute to a further refinement of these systems and the development of safety margins for the tensioning of large gilt leather surfaces. To begin with further mechanical testing is required (strength, elasticity and elongation of aged gilt leather), as well as studying sorption behaviour and dimensional changes as a response to changing climatic conditions, as a function of ageing (condition), manufacturing characteristics (e.g. type of tanning, type of leather, degree of tooling, etc.), and different tensioning systems. Standard physical tests are easy to perform on new leather. These are however less suited for historical gilt leather as they are destructive. Research is needed to develop micro-analytical non-destructive tests that are comparable with standard test methods. A better understanding of the correlation between chemical and physical condition also needs to be established.

Evaluation and monitoring
The evaluation of tensioning systems that have been put in place in the past 10-15 years, and their possible effect on the gilt leather wall hangings (stretching of the top part) is of importance. Next to these evaluations, a methodology for monitoring gilt leather objects after conservation is essential to understand whether treatments are effective. After installing a non-original hanging system, the wall hangings should be monitored for deformation, stretching, tears, stress and craquelure. The effects of strain, due to RH changes, on the leather, as well as the decorative layers of gilt leather, need to be addressed by developing a monitoring system. How much strain can the gilt leather take before cracking occurs in the leather, silver leaf, varnish and paint layers? Results of *in-situ* monitoring should be compared with a controlled laboratory set-up with historical gilt leather, in order to fully understand the influence of the climatic conditions, and also flexible tensioning systems, on the gilt leather object.

Climate and wall protection
Little is known about the micro-climates behind wall hangings. Recent research points to the significant role of temperature gradients in the degradation of oil paint on canvas wall hangings. Different types of wall protection or backings have been installed behind gilt leather wall hangings. Humidity buffering backing materials (e.g. wood panelling) are often applied, with the intention to avoid sudden relative humidity changes. The effect of these backings on micro-climates behind gilt leather wall hangings has not been studied so far. In depth research is needed to be able to create optimal environments for wall hangings situated in monuments. For both research topics, the monitoring of physical changes of gilt leather objects and the monitoring of climate and micro-climates in-situ, collaboration should be sought with the NWO Climate4Wood project.

Conservation materials
Knowledge on conservation materials for application in structural repairs and (strip) linings has been developed within other conservation disciplines (textiles, leather and paintings). Some testing of commonly used adhesives and repair materials for gilt leather has been done. However conservators would benefit from further mechanical testing, especially in the case of strip linings, which are applied whenever one needs to attach a wall hanging to a tensioning system. The development of consolidants and adhesives for application in gilt leather conservation, taking into account the specific requirements posed by its individual materials, would be beneficial. Additionally risk analyses for the use of certain solvent and water based adhesives, of repair materials and of application techniques (for example using heat), for the decorative finishes on gilt leather should promote a safer use of these techniques and materials.

Within NICAS a project on the development of specific conservation adhesives (Hans Poulis, René de la Rie) has started. Collaboration with this research initiative could result the development of requirements for custom-made adhesives for the use on gilt leather.

Surface cleaning techniques
The conservation of the decorative finishes of gilt leather has received surprisingly little attention over the past years. Certain gilt leathers with a heavily darkened painted surface could benefit from the advanced surface cleaning techniques developed recently within the realm of paintings conservation. However special attention should be paid to both the leather support, which is very porous, and to the specific ground layers of gilt leather consisting of animal glue, silver leaf and a yellow- or orange-brown oil-resin varnish, which is ‘solvent-sensitive’. Special care should also be paid to the

glazes and other semi-transparent paints, as well as possible original varnishes on certain paints and glazes. Surface (solvent) cleaning of gilt leathers may be compared to partial varnish removal on paintings, a practice that is still very much in development and researched at the moment (techniques, methods and monitoring).

Corrosion of the silver leaf seems to be an irreversible process for which preventive conservation measures still need to be developed. Possible directions are the control of climatic conditions, as well as the development of protective coatings. Degradation phenomena and processes, and the influence of climatic conditions, need to be better understood before any of these measures can actually be developed. Localized electrolytic cleaning of silver tarnish seems promising for the sub-type of silvered leathers. Further research and development is needed to ensure a safe use of the tools and techniques.

Conservation history

Conservators have observed irreversible damage to the decorative surfaces of gilt leather, caused by past restoration treatments (19th and 20th century), such as leather treatments (with oil dressings or emulsions), surface treatments using solvents (cleaning, re-varnishing and even paint stripping as a result of misunderstandings). Oil resin varnishes and oil paints may have altered (softening and darkening) both physically and chemically, which may cause unexpected behaviour during future conservation treatments.

There is a great need for an overview of past trends, techniques and materials in the conservation of gilt leather. A comprehensive study and overview will create awareness amongst conservators of the possible presence of certain materials on the objects (such as oils, waxes, non-original varnishes, linings, etc.) and create understanding of (permanent) changes in appearance, such as darkening or change in gloss. The study of the effects of such previous conservation treatments should be examined further to be able to adapt current conservation and develop preventive conservation measures.

Awareness and dissemination of knowledge

Communication of the do's and don'ts in the conservation of gilt leather, in various languages, is urgently needed. Some curators, conservators and architects are not aware of the extreme vulnerability of the material, and the related conservation difficulties, neither of the risks of certain conservation treatments to the specific materiality of historic gilt leathers. Due to the large variety of materials in different gilt leather objects the importance of thorough diagnostics and custom conservation treatments should be underlined. Also more attention should be paid to previous restorations and the risks they pose when performing new conservation and restoration work. Both preventive conservation and the role of the physical environment of gilt leathers should be brought to the attention as well. A simple digital platform that communicates conservation guidelines, and disseminates best and worst practices (from individual conservation cases), requires a limited input of resources and will yield enormous positive long term effects.

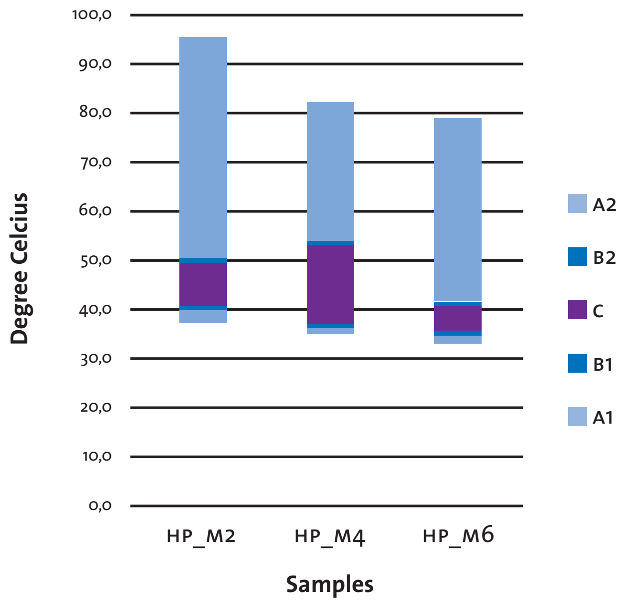
Training in conservation of gilt leather should be optimized. In order to train the students well, the trainers should be trained sufficiently too. "Train the trainers!" An international summer school of some sort could be organized to promote interdisciplinary teamwork and to increase knowledge exchange on gilt leather across the borders.

RECOMMENDATIONS FOR NICAS

The research topics for the improvement of the conservation of gilt leather are vast and diverse, and overlap with other conservation disciplines. Possible connections should be made with other research activities, with gilt leather included as a case-study or focus area, for example in the NICAS project on conservation adhesives, the NICAS-project on organic coatings on metal, or the Iperion project.

A future NICAS gilt leather project should focus on the material dynamics and conservation issues that are very specific to gilt leather, such as for example tarnishing of the silver leaf, the hygrometric response of leather and decorative layers, and degradations due to conservation treatments with oil. As a large percentage of the gilt leather hangings are not kept in controlled museum environments, it seems a logical choice to study the physical behaviour of gilt leathers in response to environmental conditions. An integrated approach is desirable, which includes connecting the physical and chemical behaviour of the different material layers of gilt leather. This research should result in the development of diagnostic tools for conservators, safety margins, risk profiles, and preventive conservation guidelines.

DIAGNOSTICS



68 Bar graph showing shrinkage temperature measurements of three samples of historic gilt leather (Sint Pietershof Hoorn) that are represented in hydrothermal stability profiles. Sample HP_M2 has the highest TS (40.2°C) which corresponds to the low end of medium deterioration. The other two samples have a TS below 40°C, placing them in the beginning of a heavy damaged condition.

Systematic material analysis of gilt leather has only been performed recently. In the past material characterization was mostly connected to individual conservation projects, though limited in number. Studies involving a larger representative corpus of gilt leathers, characterizing all the different material layers are few, and up until now the focus has been on determining source materials and production processes, i.e. art technological research. Systematic characterization of degradation phenomena and processes has not yet been undertaken for the particular material build up of gilt leather. In related fields, such as leather and paintings conservation, the state of the art of diagnostics is well advanced. For sure knowledge from these areas can be applied or transferred. However the typical composition of gilt leather is such – leather substrate, silver leaf and coloured oil-resin varnish as most distinguishing features – that material dynamics are very specific as well.

The following chapter will describe the diagnostic tools and techniques currently used for gilt leather. Subsequently the potential of additional complementary diagnostic techniques will be discussed in the light of studies into degradation phenomena and the development of new conservation treatments.

OVERVIEW OF DIAGNOSTICS APPLIED FOR GILT LEATHER

Leather

Advanced research projects into the degradation of leather took place in the 1990's. Already from the 1970's onwards diagnostic tools have been developed and applied to the condition assessment of leather. These were chemical tests measuring pH, ammonium sulphate, fat content, moisture content and determining the tanning method, based on methods developed by the American Leather Chemists Association (Hallebeek 1980). The Central Research Laboratory for Objects of Art and Science in Amsterdam – the predecessor of the Cultural Heritage Agency –played a major role in this analytical approach. The tests were performed using relatively simple laboratory equipment, some of which could also be used in a conservation studio. During the STEP leather project, discussed before, methods for condition assessment of leather were refined and further developed (Larsen 1996). Current indicators of the rate of deterioration of the leather are shrinkage temperature, combined with acidity tests. Shrinkage temperature is defined as the temperature at which leather fibres experience hydrothermal denaturation. According to the standard test method leather fibres are wetted thoroughly and heated, observed under the microscope, while temperature is recorded. Shrinkage of the fibres indicates the start of hydrothermal breakdown. Shrinkage temperature and acidity tests are used in gilt leather conservation, to determine the state of degradation of the leather, to indicate to which extend heat and humidity can be applied during conservation treatments. The shrinkage temperature (TS) of new vegetable tanned leather is between 70°C and 90°C, depending upon the type of tannin, and the TS of heavily degraded leather can be as low as 35°C (figure 68).

During the STEP and ENVIRONMENT leather project analytical techniques, such as HPLC and optical density, have been applied to identify and quantify degradation products of the protein-tannin complex of leather fibres (Larsen 1994 and 1996). Damage assessment of protein collagen (in historic parchment) has been performed at different structural levels – macroscopic, microscopic, mesoscopic and nanoscopic – using a wide range of analytical techniques (Larsen et al. 2002 and 2005), such as light microscopy and scanning electron microscopy (SEM), atomic force microscopy (AFM), Differential Scanning Calorimetry (DSC), x-ray diffraction (XRD), Fourier transform Raman spectroscopy (FT-Raman), solid-state nuclear magnetic resonance (NMR), HPLC, electrophoresis and Liquid Chromatography – Mass Spectrometry (LC-MS). However all these methods failed to provide a better overall understanding of degradation because there were too many variables involved. To overcome this problem an international database for degradation patterns of historic parchments was set-up with the goal of comparing data in a sound statistical way (Larsen 2008). Unfortunately the database in not maintained anymore because of a lack of funding.

There is still a need for a deeper understanding of the diagnostics needed to establish condition and to embed this into routine standard condition tests to be brought into the field to be carried out by bench conservators. The diagnostic test of the degree of cohesion of the leather fibres, developed by the School of Conservation in Copenhagen, is a good way of establishing physical condition. In the Netherlands however diagnostics of leather fibre condition by shrinkage temperature measurements is unfortunately not practiced, simply because the equipment (micro hot table) is too expensive for independent conservators. Differential scanning calorimetry (DSC) is also not accessible for conservators in the Netherlands.

The type of animal skin can say something about the provenance of a gilt leather. Determining the DNA of leather is problematic as the structure of the proteins is altered by the tanning processes. Kirby has succeeded in determining the animal species by using Peptide Mass Finger Printing (PMF) (Kirby et al. 2013). With this technique a protein sample is prepared with enzymes in order to break it down into peptides which are measured by mass spectrometry. The identification of the animal species is based on seven different peptide markers. Within the French CORDOBA project, introduced previously, the animal species of different gilt leather samples have also been identified with PMF. Only animal species can be determined, not the breed.

Current research in leather and leather production techniques is predominantly performed at the Institute for Creative Leather Technologies (ICLT) at the University of Northampton (UK). Research on conservation related topics is done in collaboration with the Leather Conservation Centre (Northampton).

Decorative layers

The generally accepted technique to study the decorative layering of gilt leather is by examining cross-sections with light and UV-fluorescence microscopy, and other complementary techniques such as Scanning electron microscopy – Energy-dispersive x-ray spectroscopy (SEM-EDX) and Fourier transform – infrared spectroscopy (FT-IR). They deliver detailed information on the layering (light and UV microscopy), and elementary composition of the different organic (FT-IR) and inorganic components (SEM-EDX) within the layers, such as the metal leaf and the pigments of the paint layers. They can also show irregularities within the different layers, which may point to certain degradations. In several cases of severely degraded gilt leather, light microscopy (UV) showed extreme deformations of the oil-resin varnish and the paint layers, suggesting a possible damage by past restoration treatments with oils or solvents (Posthuma de Boer 2012, also observed by Van Velzen in 2015) (figures 48, 61). Microscopic examination of cross-sections aids in answering art technological questions, as well as questions about degradation phenomena. However it is an invasive technique, depending on the size of the sample taken, which can only yield location specific information.

Glue layer

Current literature states that fluorescence microscopy is an unreliable technique for identifying glue layers in gilt leather cross-sections (Schulze 2011). It is unclear why the glue is sometimes visible as a fluorescing layer, and in other cases not. With SEM backscattered electron (SEM-BSE) images however the glue layer can be readily distinguished (Posthuma de Boer 2012). Up until now no other analytical techniques have been tested to identify the type of glue (both egg-white and parchment glue are mentioned in historical literary sources). Nor have the properties of the glue, and possible degradations, been related to certain degradation phenomena.

Metal leaf

The elemental composition of the metal leaf can be characterized by x-ray fluorescence (XRF) and SEM-EDX. These techniques are rather limited when one wants to identify trace elements in the silver, such as for example lead, mercury and copper. Talland et al. analysed the composition of the silver leaf of several Northern European and several Southern European gilt leathers with proton-induced x-ray emission (PIXE) (Talland et al. 1998), which provides quantitative data for major and trace elements. Two samples of gilt leathers from the Netherlands, and four samples of Spanish or Italian gilt leathers from the collection of the Isabella Steward Gardner Museum, Boston (USA), have been analysed. The results show that the Netherlandish gilt leather samples contained approximately 90% silver, whereas for the Southern European gilt leathers approximately 95% silver content was measured. Gilt leather from the Netherlands contained a significantly higher percentage of lead content than the Southern

European ones. These results suggest that trace elements in the silver composition could be used as an indicator of provenance.

Preliminary results of the research project CORDOBA have recently been presented during a gilt leather seminar in France (Radepont et al. 2015). PIXE – Ion beam accelerator AGLAE, Louvre, Paris – has been used by Radepont to determine the composition of the silver leaf, which was combined with Rutherford Backscattering Spectrometry (RBS) to measure the thickness of the silver leaf (Radepont et al. 2015). These properties were expected to serve as chemical and physical markers for geographical provenance. Forty five samples of gilt leather from Italy, France, The Netherlands and Spain, from the 16th-18th century have been analysed.

Regarding the trace elements in the silver, the French researchers followed a different methodology. With PIXE all the elements in the different layers of the sample are detected. Sometimes it is not clear whether the element detected was present in for example the leather, or as a trace element in the silver leaf. Elements that are unlikely to be found in other layers, and can be related to the mining or production of gilt leather are mercury and gold. The percentages of these trace elements and the percentage silver content were measured. It has proved difficult to relate these outcomes to gilt leather manufacturers, mainly because of the limited amount of gilt leather samples taken.

RBS measurements indicate that the thickness of the silver leaf is on average 100 nm, but varies a lot within a range of 50 to 250 nm, depending on different factors, such as the superposition of different leaves, surface roughness, porosity or irregularities resulting from burnishing or tarnishing. A general trend was observed indicating that Dutch gilt leathers were made of a thicker silver leaf. However more Dutch samples need to be analysed to confirm this. The dimensions of the silver leaf of these different gilt leather samples were also compared. This indicated that gilt leathers from a later period have larger silver leaves. Earlier Italian and Spanish gilt leathers do have smaller leaves. Application techniques during production may play a role in these differences in dimensions.

Future research within this project will concentrate on further thickness measurements, and developing RBS cartography methods in order to map the varying thicknesses of the silver leaf for a larger surface. Degradation of the silver leaf is the topic of the research project CORD'ARGENT running in 2016. This involves studies into the rate of corrosion of the silver leaf, as a function of characteristics such as composition, porosity, and degree of burnishing. Aside from the characteristics of the silver itself, the impact of organic components on corrosion processes is being investigated, as well as the influence of products used in restoration treatments.

Oil-resin varnish and paint layers

One of the current diagnostic challenges regarding the oil-resin varnish is to identify and quantify all the components of the coloured natural oil-resin varnish. Historic literary sources indicate that a large variety of soft and hard natural resins may have been used (Schulze 2011). Also a large variety of colouring components are mentioned, sometimes characteristic for a certain region of production. Pyrolyse Gas chromatography–mass spectrometry (GC-MS) is an appropriate technique for identifying different oils and resins, the main constituents of the oil-resin varnish, and as such has been used in numerous research projects (Schulze 2011, Posthuma de Boer 2012 and Robinet 2015). However the proportions of these components are difficult to determine. Moreover typical colouring ingredients, such as aloe, saffron, asphalt or dragons blood, are difficult to characterize with GC-MS (Schulze 2011, Robinet 2015). Complementary analytical techniques, such as HPLC, could help to distinguish between different recipes of oil-resin varnishes. French researchers have been using Synchrotron FTIR and Fibre Optic Reflectance Spectroscopy (FORS)-visible light (VIS) and near infrared (NIR) to identify organic components (Robinet 2015).

GC-MS has been applied successfully to detect traces of components from restoration products, such as non-drying oils of animal origin, beeswax, rapeseed oil and lanolin, in the oil-resin varnish (Posthuma de Boer 2012, Robinet 2015).

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is a surface analytical technique providing elemental and molecular information, which has recently been used for the analyses of organic substances in archaeological and cultural heritage artefacts. It was used to identify organic pigments and components of the gold varnish of a gilt leather altar frontal from the San Domenico church in Orvieto (Italy) (Tortora et al. 2014). The presence of indigotin in a blue paint layer, colophony resin in the gold varnish and the corrosion products silver oxide and silver chloride on the silver leaf have been positively identified with TOF-SIMS. It is a promising technique which might be used to identify organic colourants in the gold varnish, and silver tarnishing products on uncoated silver leaf. Recently introduced Mass Spectrometry Imaging (MSI) techniques may also give a solution for the detection of organic components that were not detectable so far.

In collaboration with the RWTH Aachen University (Germany) and the College of William and Mary (USA), SRAL has performed single-sided NMR studies on cured oil paint layers to comparatively examine solvent penetration and the relative changes in mechanical properties resulting from varnish treatments (Fife et al. 2015). This non-destructive portable technique may also be of interest for studying the effects of surface solvent treatments, or other restoration interventions, on the painted layers of gilt leather.

Surface topography

The RICH project (Reflectance Imaging for Cultural Heritage, Centre for the Study of Medieval Art, in collaboration with the department of electrical engineering (ESAT) and the Imaging Lab, KU Leuven, Belgium) started in 2013 with the development of a micro dome (diameter 33 cm) to monitor the topography of artefacts (Watteeuw 2014). The hemispherical shaped imaging device digitizes with multi-directional lighting. The module has 226 LED-lamps evenly spread across the inside of the hemisphere and a single downward looking video camera (28 million pixels). After processing, through virtual relighting, fine details can be highlighted by the use of specific digital filters, bringing out structures that are not visible under single illumination. Fine measurements and 3D surface profiling (max. dimension of the object is 12 to 18 cm) can be generated through the application and exported to 3D.

A second multispectral micro dome can explore pigment characteristics in the painted surface (Watteeuw et al. 2016). On-going software development (2016-2020) explores shape recognition of stamps and imprints in artefacts, a method that can contribute to research in use and degradation of the corpus of stamped panels, and compare flaws and variation of imprints.

Techniques used in the RICH project, Reflection Transformation Imaging (RTI) or more specific Photometric Stereo, can be used to study the topography of gilt leather. The visualization technique with the portable micro dome offers the possibility to monitor and visualize stamps motifs in gilt leather, to monitor in the X, Y, Z – ax and measure and compare them in great detail.

POTENTIAL OF NEW DIAGNOSTIC TECHNIQUES

As has been described above the material characterization of all the different organic and inorganic components of gilt leather requires an approach where different complementary analytical techniques are combined. The French projects CORDOBA and CORD'ARGENT so far show very promising results. Within these projects the importance of non-destructive techniques is underlined, and the opportunity of performing higher resolution measurements is taken, using existing analytical techniques for a particle accelerator and a Synchrotron. However other non-destructive analytical techniques have recently been applied for material characterization of cultural heritage that are more easily accessible (costs of the equipment are significantly lower), and offer the opportunity of visualizations or mappings on a macro-scale. Hyperspectral Imaging (HSI) and Optical Coherence Tomography (OCT) are optical techniques that either have potential in characterizing materials and degradation phenomena by optical properties, or in determining and visualizing mechanical properties and behaviour of materials, including defects. Below these techniques are briefly explained, and the potential for applications in cultural heritage is described. Lastly some techniques currently used in corrosion studies, such as Electrochemical impedance spectroscopy (EIS) combined with recently developed spectroscopic techniques, such as grazing-angle Fourier Transform Infrared (FTIR) spectroscopy, are briefly explained to explore possibilities for an in depth study of the different degradation processes related to the corrosion of the silver leaf.

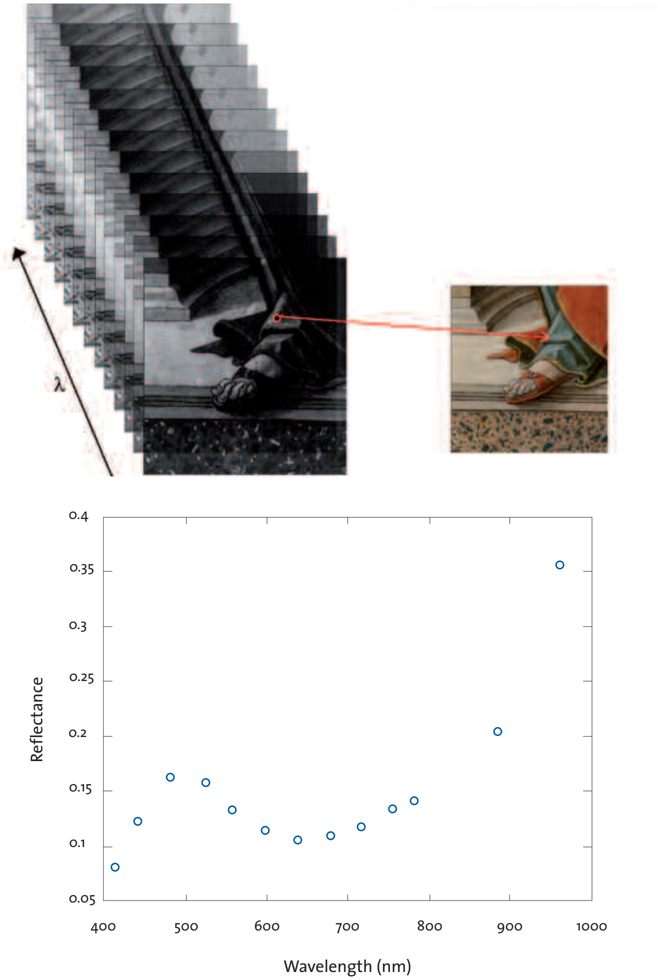
Hyperspectral Imaging

Hyperspectral Imaging (HSI) is an optical analytical technique that combines digital imaging and spectroscopy. It captures optical images of different wavelength ranges of the electromagnetic spectrum (e.g. UV, VIS, and IR), and at the same time collects the spectral reflectance for each pixel. This results in a so-called 'image cube' or 'spectral cube' containing images for a series of spectral windows, and reflectance spectra for each pixel (figure 69).

Hyperspectral imaging was first applied in astronomy, but has now a wide range of applications, for example in biology, chemistry, medicine and quality control. Within the domain of art history, archaeology and conservation, hyperspectral imaging has been used since the 1990's, mostly for the examination of paintings and manuscripts (Liang 2012). It has proved a successful tool for revealing things that are invisible to the naked eye. The near infrared spectrum (700-2500 nm) can be used for revealing underdrawings. To make faded writing in manuscripts visible UV-reflected light and certain infrared bands are used. Retouchings can be made visible this way as well. With hyperspectral imaging it is possible to make accurate colour images, independent of lighting and viewing angle, and as a result colour changes can be recorded. Hyperspectral imaging can also be of use in the monitoring of conservation treatments, for example monitoring the thickness of remaining crusts on marbles during laser cleaning (Papadakis at al. 2010). For monitoring the partial cleaning of (yellowed) varnishes hyperspectral imaging has proved applicable as well (Kubic 2007).

Another interesting application is pigment characterization, which unfortunately remains complicated, as some pigments do not have very distinct spectral features, for example yellow pigments (Kogou et al. 2015). Characterization of pigment mixtures is a challenge, but has been done (Liang 2012). Public reference data (reflectance spectra) for different types of pigments, binders and substrates exist. However people still tend to make their own reference databases, as spectra are dependent on many complex factors, such as the effect of particle size of the pigment, the pigment to binder ratio, the type of binding medium, the type of substrate and the effects of natural ageing. Furthermore surface dirt and a yellowed varnish may also have an effect on the recorded spectrum. UV-fluorescence images and fluorescence emission can be obtained by certain hyperspectral imaging systems, providing an opportunity for the characterization of varnishes.

Hyperspectral imaging is non-invasive as it does not involve taking micro-samples of the art object. However depending on the experimental set up, it may involve high intensity illumination, which also produces high temperatures. Special care needs to be taken when examining light or heat sensitive pigments and materials. The strategy taken by some researchers in the past is to choose higher light intensities, in order to minimize the exposure and imaging time. The reasoning behind this is the assumption that



69 Schematic diagram illustrating a spectral cube obtained from multi-spectral imaging. The colour image derived from the spectral cube and a spectrum for a point on the blue colour which can be identified as the pigment azurite.

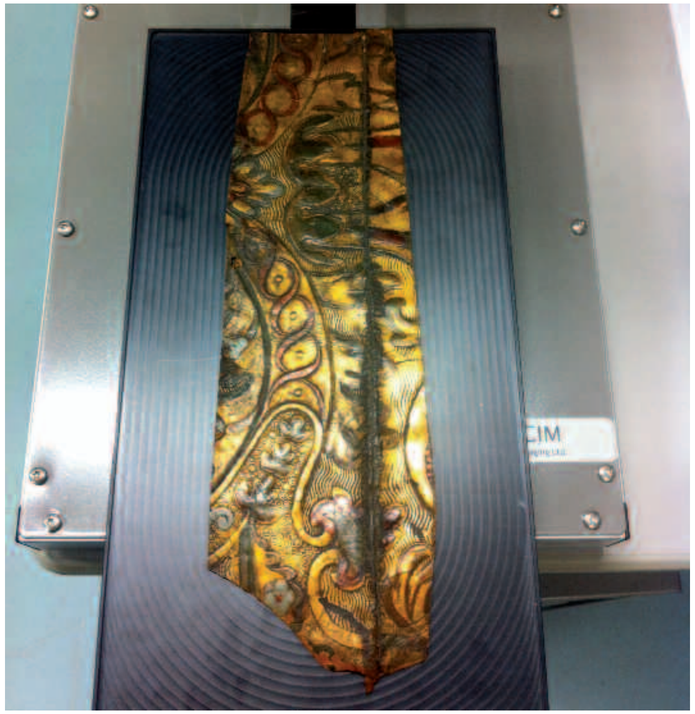
the reciprocity principle holds, that is most light induced damage to objects is determined by the total accumulated energy the object is exposed to, not by light intensities as such. However recent studies have shown that reciprocity principle can break down (Liang 2011). The strategy of maximizing light intensities, and minimizing imaging time only works to a certain extend. If one wants to scan larger areas of an object, and maintain a high image scanning resolution, it is difficult to keep illumination time limited. When working with light and heat sensitive objects, one has to consider changes in the hardware set-up, such as for example limiting the area that is exposed to light, or considering different types of lamps. However, with the improved sensitivity of modern detectors, the requirements for high intensity illumination has been greatly reduced.

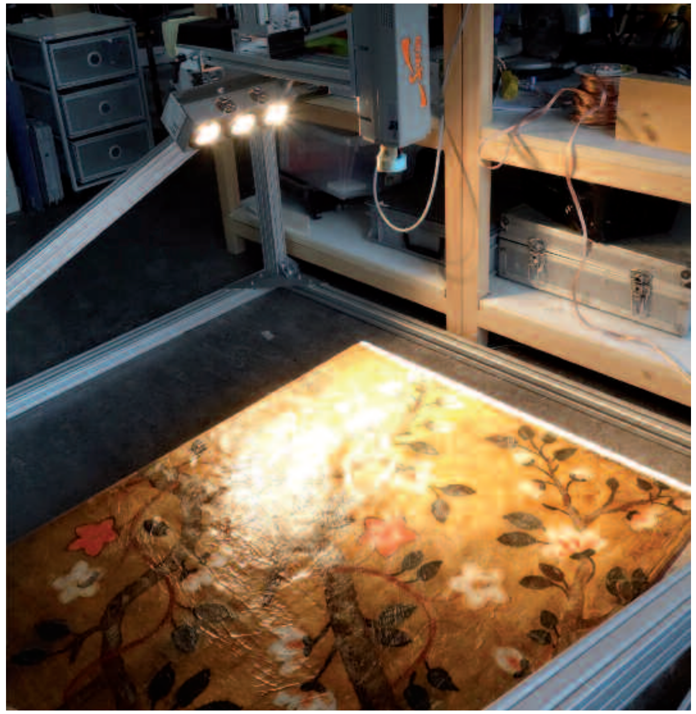
Hyperspectral Imaging has the capability to spatially map certain pigments present in gilt leather (figures 70-73). It potentially gives information on degradation phenomena, such as pigment degradation and the spatial distribution of the corrosion of the silver leaf. To perform this analysis advanced imaging processing tools, such as the TUD Image Processing Platform (TIPP) (Papadakis et al. 2016), are required.

Optical Coherence Tomography

Optical Coherence Tomography (OCT) is a non-invasive analytical technique originally used for medical diagnostics, specifically for imaging of the eye in ophthalmology. From the early 2000's it has been further developed for use in technical art history and conservation. Different OCT systems exist, including time-domain OCT (TD-OCT) and frequency-domain OCT (FD-OCT), all operating by means of near-infrared light and interferometers. The light is partially reflected at interfaces of different refractive index, or sometimes scattered in places where the structure is not homogenous. The reflected and scattered light is collected, and the propagation distance of the returning light is measured by low coherence interferometry (Targowski et al. 2010). The data from these measurements are then used to construct 2D or 3D images – tomograms – which show surface and subsurface structures (figure 74).

OCT has found several applications in art and archaeology. The first and most obvious is the non-invasive examination of the stratigraphy of paint and varnish layers. As such it has proved useful in the revealing of underdrawings, signatures, overpaint or retouchings. The potential of OCT for the use in conservation treatments has been explored, for example for the monitoring of laser or solvent cleaning of varnish on paintings. The thickness of different layers can be measured, which may aid in cleaning processes. The mechanical behaviour of materials in reaction to environmental conditions can be visualized and monitored by means of OCT as well. A last interesting application is the measurement of refractive indices of different varnish layers (Liang et al. 2007). In recent work OCT has been combined with Hyperspectral Imaging for the



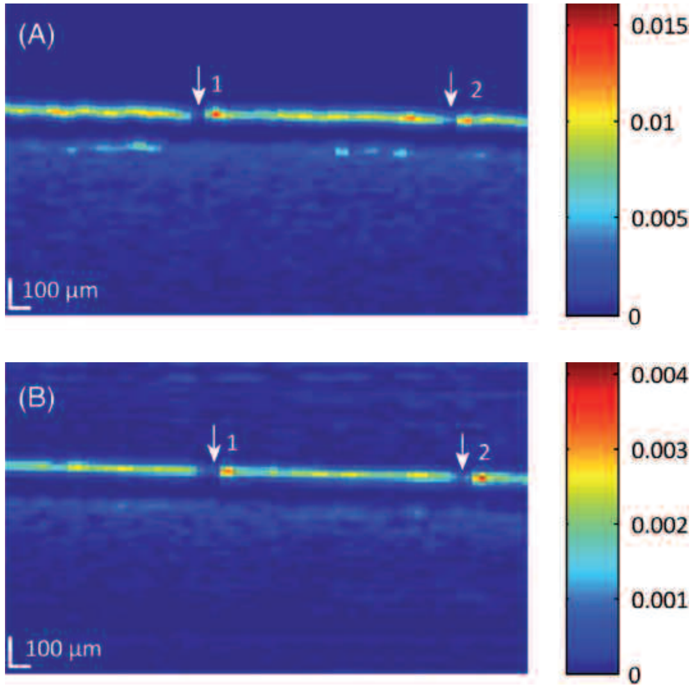


70 A gilt leather fragment from the Rijksmuseum Amsterdam on the scanning platform under a hyper-spectral imaging camera.

71 The hyperspectral imaging setup at Delft University of Technology.

72 The hyperspectral camera mounted on an automated 3D scanning plat-form, developed at Delft University of Technology.

73 Close-up of the setup in the con-servation studio at SRAL, gilt leather wall hanging from the town hall in Maastricht.



74 Cross-sectional images taken from an epoxy coating on a carbon-fibre composite measured by (A) TD-OCT and (B) FD-OCT. The arrows indicate the locations of micro-cracks within the coating.

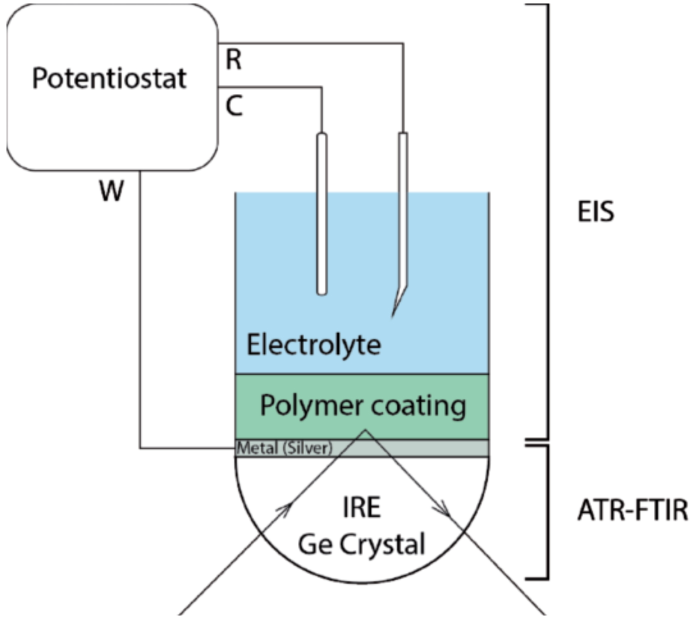
mapping of coating thicknesses (Dingemans et al. 2015). OCT has also been used for 3D imaging of the follicles in a leather cover of a 9th century bible retrieved from a bog (Liang 2011).

OCT is a technique that is mostly suitable for stratigraphic applications directed at visualizing internal structures. It is however limited to materials that are partially transparent to the incoming light, such as porcelain, paper, parchment and varnishes or other (semi-) transparent coatings (Targowski et al. 2004). Long wavelength beams of light have also been used and they are able to penetrate deeper into the material (Liu et al. 2014a). OCT has a depth resolution of 1-10 micrometers. OCT is particularly sensitive to refractive index discontinuity and as such it is the most sensitive method for mapping the different thin varnish layers (Cheung et al. 2015). When interpreting these so-called 'virtual' cross-sections, one has to bear in mind that it gives information on the reflection, scattering and absorption properties of the material. As such tomograms are rather different than physical cross-sections examined by microscopy.

OCT is interesting for gilt leather as it can measure paint and varnish layer thicknesses. Other applications of OCT for gilt leather could be the detection of hair follicle patterns in the leather to determine the type of leather and 3D stamp registration (scanning) by means of combined 3D surface profiling, HSI and OCT measurements. One interesting application already demonstrated is the surface profiling of the front and back surfaces of a wooden panel painting to assess holes and cracks in the wood (Liu et al. 2014b). A similar approach could be used to assess punch marks. Combining OCT and HSI allows for 2D and 3D damage mappings, relating chemical and physical changes, that are often invisible to the naked eye, or are variable with human perception. This is however challenging from the perspective of 3D data fusion. Degradations that are interesting to investigate with these techniques are: silver corrosion, pigment degradations, varnish discolourations and deteriorations, crack patterns in the different material layers, and delamination between different layers.

Electrochemical, spectroscopic and surface analysis techniques

Within materials science and engineering, corrosion mechanisms and adhesion and delamination of protective coatings on metals, have been studied extensively for applications in the automobile, aerospace, shipbuilding and construction industries. Some of these analytical techniques could be of interest for the study of material dynamics in gilt leather, especially those for corrosion processes of the metal leaf, delamination between different material layers, and increasing porosity of the oil-resin varnish coating on the silver. Techniques of interest are electrochemical impedance spectroscopy (EIS), combined with recently developed spectroscopic techniques, such as grazing-angle FTIR spectroscopy, local surface potential measurement techniques, like scanning Kelvin probe (SKP), Raman spectroscopy and surface analytical techniques, such as X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES).



75 Schematic drawing of integrated EIS with ATR-FTIR set-up to study the silver-polymer interface based on Kretschmann geometry.

Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is a conventional AC electrochemical technique which is commonly used for in-situ monitoring of water uptake in organic coatings, for studying degradation of polymer films and corrosion (Zhang et al. 2007, Soer et al. 2009 and Heyer et al. 2014). Impedance measurements are based on modelling of the system as an electrical circuit. The model normally consists of resistors representing resistance of the solution, coating and polarization resistance of the system and capacitors as the dielectric part of the organic film or double layer capacitance. EIS uses very small potential perturbation signals and records the small electrical current response of the system, which does not disturb exposure conditions. It is also possible to use low conductive solutions which are important for studying specimens like gilt leather.

Combined spectroscopic techniques

Combined grazing-angle Fourier Transform Infrared (FTIR) spectroscopy or Raman Spectroscopy and XPS or AES surface analytical techniques may provide information about the bonding mechanism and the bonding strength of very thin (remnant) coatings. This may aid in understanding the adhesion and degradation of the polymer film to the underlying silver layer in gilt leather. Additionally, the dynamic adsorption and polymerization processes of monomer and polymer coatings can be characterized by reproducing samples of these systems for testing.

Investigation of the polymer-metal interface is challenging when the interface is masked by a relatively thick coating. An integrated spectro-electrochemical setup has been developed that combines attenuated total reflection FTIR (ATR-FTIR) based on Kretschmann geometry measurements with EIS (figure 75). This method is used to study the bonding mechanism and degradation of polymer layers for different coating systems (Taheri et al. 2013a-c). It has the advantage of providing information from a metal-polymer interface. The interface is studied from the metallic side, by a laser light in the infrared region. It is reflected from an internal reflection element (IRE), a Ge or ZnSe crystal producing an electrical field that passes into the metallic film and medium in contact with the IRE. This method can be introduced to study gilt leather and give valuable information about the degradation of the coating, interfacial bonding and degradation mechanisms of the silver/polymer interface.

Characterizing degradation and corrosion at the interface

The Scanning Kelvin Probe (SKP) is a non-destructive instrument designed to measure the surface work function difference between conducting, coated, or semi-conducting materials and a metallic probe. It can evaluate and quantify ion mobility along the metal-polymer interface and their delamination with high local resolution. Moreover, the Volta potential variation due to pre-treatment of the metal can be evaluated both on objects and reconstructions. One of the main advantages of performing SKP measurements is the possibility to do the experiment in air (Stratmann and Streckel 1990a and -b). This attribute makes SKP a very suitable technique for atmospheric corrosion studies rather than exposing a sample to non-representative electrolytes. Also, this technique has the possibility to scan over the surface to measure the local potential in different areas which is important to study corrosion in presence of a defect in the organic coating and measuring delamination rate due to penetration of water molecules or aggressive ions from the defect to the intact area of the coating (Stratmann et al. 1996). Therefore, this technique has the possibility to measure the changing corrosion resistance of the silver leaf in gilt leather and degradation of the polymeric film in different atmospheric condition e.g. wet, dry and the effect of the atmospheric contamination.

Tomography techniques could potentially help to further characterize the interface between paint systems and their metal substrate by examining and visualizing delamination and corrosion phenomena not visible from the surface.

Electrochemical, spectroscopic and surface analysis techniques offer possibilities for the identification of the protective polymer coatings on silvered leathers (in collaboration with NICAS project *Organic polymers on metal substrates*). They may also provide a better understanding of corrosion processes of the silver leaf and the interaction with the degradation of polymer coatings (glue and oil-resin varnish layers).

CONCLUSIONS

For certain material components of gilt leather, such as leather and silver, state of the art diagnostic techniques are being used and methods have been developed for material identification, the characterization of degradation, and for condition assessment. For other materials, such as the protein based adhesive and the oil-resin varnish layers the appropriate diagnostic techniques have to be selected and tested yet and methods have to be developed still. For example TOF-SIMS and Mass Spectrometry Imaging techniques could be interesting for identification of the colouring components of gold varnishes, in addition to the commonly used GC-MS which is limited in its detection of certain compounds.

Some researchers (Bonnot-Diconne et al. 2014, Robinet 2015) have started developing a methodology for the characterization of all the material layers in gilt leather, using multiple analytical techniques. The use of the AGLAE ion beam accelerator, has proved powerful in delivering information on a molecular level, in addition to the more commonly used analytical techniques. Ideally this methodology should be complemented with other non-destructive diagnostic techniques that deliver information on a micro- and macroscopic scale. As has been indicated above, this requires a selection and testing of state of the art and new diagnostic techniques, and the development of testing and measuring protocols, for each of the materials of gilt leather, and the development of appropriate image processing tools. The complementarity of various non-destructive imaging and spectroscopic techniques has been examined in the context of paintings (Kogou et al. 2015) which can be appropriated for gilt leathers. Preferably this should be done within a larger European consortium of partners.

Easy to use, portable and affordable

From the conservator's point of view, there is a need for easy, portable and affordable diagnostic tools for characterizing and assessing the degradation levels of the various materials that gilt leather consists of. Special attention should go into making certain tools accessible to conservators. These easy diagnostic tools could also be provided to non-conservators, people involved in heritage organisations like museums and historic buildings, with the purpose of raising awareness of degradation processes.

RECOMMENDATIONS FOR NICAS

For a future NICAS project the challenge is to find the appropriate complementary analytical techniques that, when combined, will be able to characterize all different organic and inorganic materials of gilt leather. The advantage of non-destructive optical techniques, over the currently used ones, is that they are non-destructive, give information on a larger area, are able to detect both on a micro and macro scale, are able to reveal subsurface characteristics and allow for different kinds of visualizations. As there might be a lot of time involved in the development of testing and measuring protocols when applying new analytical techniques to gilt leather, they need to be carefully selected on the basis of their distinct features. For example hyperspectral imaging has the capability of mapping pigment and other material degradations, which has a clear added value when combined with for example macro XRF-scanning.

The challenge is to offer a real integrated approach, where diagnostic development and research questions from an art historical or conservation perspective are both addressed. Development of diagnostic tools should ideally result in easy to use, portable and affordable equipment that in the long run can serve conservators as well. If equipment cannot be taken out of a laboratory setting, creating accessibility of diagnostic equipment to conservators for the material characterization and condition assessment of gilt leather materials should be considered.

APPENDICES

APPENDIX I
Symposium on Improved conservation strategies for gilt leather
31 March 2016

Location
Bonnefanten Museum and Stichting Restauratie Atelier Limburg (SRAL), Maastricht

76 Guest speakers from the afternoon-session in the lecture theatre of the Bonnefanten Museum.

On Thursday 31st of March a one-day symposium on the state of the art in gilt leather research and conservation was organized in Maastricht. International experts from interdisciplinary backgrounds presented current conservation challenges, the state of the art in material degradation research, new art historical findings, and the potential of diagnostic techniques from different engineering fields. The programme was well attended by an audience of 60 participants of owners and custodians of gilt leather wall hangings and collections, conservators of different disciplines, conservation scientists, students and other interested parties.

PROGRAMME

10.00-12.00
NICAS Gilt Leather Project presentations
Chaired by Roger Groves (Delft University of Technology)

Roger Groves
(Delft University of Technology)
Introduction to the NICAS Gilt Leather Project.

Eloy Koldeweij
(Cultural Heritage Agency)
> Gilt leather and the art historical perspective: promising identification possibilities through technical analyses.

Bianca van Velzen and René Hoppenbrouwers
(Stichting Restauratie Atelier Limburg)
> Issues concerning the condition and conservation of the pictorial layers of gilt leather: town hall Maastricht, town hall Venlo and Lenghenhofje Dordrecht.

Martine Posthuma de Boer, **Vassilis Papadakis**
(Delft University of Technology)
> Spectral imaging of gilt leather.

Elizabet Nijhoff Asser
(RNA Amsterdam)
> Stress in leather wall hangings; mechanics, measurements and case studies.

Arjan Mol
(Delft University of Technology)
> Electrochemistry at (coated) metal surfaces.

APPENDICES

77 Bianca van Velzen, demonstrating conservation work on the gilt leather wall hangings of Maastricht town hall, Venlo town hall and Lenghenhofje Dordrecht at SRAL studios.

12.00-13.30
Lunch + demonstrations at SRAL studios

Visit to SRAL studios by Bianca van Velzen, demonstrating conservation work on the gilt leather wall hangings of Maastricht town hall, Venlo town hall and Lenghenhofje Dordrecht.

Exhibition of gilt leather reconstructions according to techniques and recipes from the 16th to the 18th century, made during a workshop at the University of Amsterdam, supervised by Martine Posthuma de Boer.

Demonstration of the Delft University of Technology Image Processing Platform (TIPP) by Jonne Goedhart and Rogier Colijn.

Demonstration of the Delft University of Technology Hyperspectral Imaging camera and set-up by Vassilis Papadakis.

13.30-17.00
Snapshots of on going research and conservation of gilt leather
Chaired by Eloy Koldeweij (RCE) and René Hoppenbrouwers (SRAL)

Andreas Schulze
(Dresden Academy of Fine Arts, Germany)
> The manufacturing techniques of gilt leather in Europe between 1500 and 1800: written art technological sources and experimental reconstructions.

Dörte V. P. Sommer
(School of Conservation (KADK), Copenhagen, Denmark)
> Ageing of historic leathers: degradation mechanisms and diagnostic tools in relation to condition assessment.

Céline Bonnot-Diconne
(2CRC)
Laurianne Robinet
(Centre de recherche sur la conservation (CRC), France)
Marie Radepont
(CRC and Centre de recherche en de restauration des musées de France (C2RMF), France)
> The CORDOBA project – silver leaf as physical and chemical marker for geographical provenance of gilt leathers? The CORD'ARGENT project – the alteration of the silver leaf in gilt leathers.

Herman Terryn
(Vrije Universiteit Brussel, Belgium, Delft University of Technology)
> Advanced surface analysis for metal art objects

Stephen Lloyd
(Derby Collection, Knowsley Hall, Merseyside, UK)
Chris Calnan
(National Trust, UK)
> Knowsley Hall's series of Old Testament paintings on gilt leather (Venice, 1656), and their conservation programme.

Abbie Vandivere, Julie Ribits
(Mauritshuis, The Hague)
> Gilded Goddess: The technical examination of a gilt leather painting.

17.00
Drinks, hosted and sponsored by SRAL.

APPENDIX II
Expert Meeting
1 April 2016

Location
Bonnefanten Museum and Stichting Restauratie Atelier Limburg (SRAL), Maastricht

78 Round table discussion during the Expert Meeting.
79 The conclusion session of the Expert Meeting
80 The participants of the Expert Meeting gathered on the stairs of the Bonnefanten Museum.

The goal of the Expert Meeting was to set the research agenda for gilt leather for the period 2017-2025. In round table discussions on each of the NICAS themes (technical art history, material dynamics, conservation treatments and diagnostics) participants were invited to reflect on the topics and themes proposed in the white paper. The discussions were led by a moderator, and minutes were made. All the gathered input has been included in the final white paper, and additional comments of the participants has been included at the draft white paper stage.

– 32 experts, 11 different nationalities
– Setting the research agenda for the conservation of gilt leather for 2017-2025

We would especially like to thank the moderators for their active involvement in leading the discussions on the different themes:

Technical Art History
Margriet van Eikema-Hommes
(Delft University of Technology and Cultural Heritage Agency, Amsterdam)

Material Dynamics
Christopher Calnan
(National Trust, Suffolk)

Conservation Treatments
René Hoppenbrouwers
(SRAL)

Diagnostics
Haida Liang
(Nottingham Trent University)

We would equally like to thank the UVA students Jazzy de Groot, Renate Oosterloo, Michelle Vergeer and SRAL intern Leonora Burton for taking minutes.

APPENDIX III

Gilt Leather Project Team

Martine Posthuma de Boer MA
(TU Delft)

Martine Posthuma de Boer is conservator-restorer and researcher of painted and decorated surfaces in historic interiors, with a specialisation in gilt leather wall hangings. She holds degrees in *Conservation and Restoration of Cultural Heritage* at the University of Amsterdam (2015), and *Art History* at the University of Utrecht (2001). Martine coordinates the NICAS gilt leather project.

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Dr Eloy Koldeweij
(RCE)

Dr Eloy Koldeweij studied History of Art. He wrote his Ph.D. on gilt leather hangings at Leiden University (1998). Since 1997 he is senior specialist on historic interiors at the Cultural Heritage Agency, and since 2015 part-time lecturer at Utrecht University.

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Dr Roger Groves
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Dr Roger Groves has degrees in Chemistry and Physics and a PhD in Optical Instrumentation from Cranfield University, UK (2002). From 2004-2008 he was a Senior Scientist at the Institute for Applied Optics, University of Stuttgart. He is currently Head of the Aerospace Non-Destructive Testing Laboratory and Assistant Professor at Delft University of Technology, The Netherlands. His research interests are in optical metrology, fibre optic sensing, spectral imaging and ultrasonics for engineering and heritage science applications. He heads the NICAS Gilt leather Project.

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Drs René Hoppenbrouwers
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Drs René Hoppenbrouwers (1961) studied Art History and Archaeology in Nijmegen and thereafter Conservation of Paintings at SRAL Maastricht. Since 1995 he worked as research conservator at SRAL and co-ordinator of the post-graduate conservation education program. In 2009 he became director and focuses on activities ranging from acquisition and research to teaching and international collaboration.

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Dr Arjan Mol is Associate Professor Corrosion Technology and Electrochemistry at the Department of Materials Science and Engineering of the Delft University. His key expertise areas are local corrosion and oxidation mechanisms of metals under atmospheric and aqueous condition, interfacial bonding of organic coatings, and development and performance assessment of smart and corrosion inhibitive coatings.

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Elizabet Nijhoff Asser
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Elizabet Nijhoff Asser is the owner of RNA – restoration of Paper and Parchment and Leather since 1986. She has degrees in Art History and in Restoration & Conservation. Her firm completed successfully the restoration of five rooms or halls decorated with gilt leather. Her speciality is the support mechanism. She is since 2012 lecturing at University of Amsterdam in the programme Restoration & Conservation of Books and Paper.

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Dr Vassilis Papadakis has degrees in Physics, Microelectronics and Optical Instrumentation. Since 2014 he works in the Aerospace NDT Laboratory at Delft University of Technology (TUD). He is also a lecturer for the BSC programme Aerospace Engineering at TUD. His research interests are in developing optical instrumentation and image processing algorithms with focus on spectral imaging for the analysis of materials deterioration.

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Kate Seymour MA
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Kate Seymour is an art historian who received a Masters of Arts in the Conservation of Easel Paintings from the University Northumbria at Newcastle (UK) in 1999. She moved to the Netherlands in 1999 to work at the Stichting Restauratie Atelier Limburg (SRAL), Maastricht as a painting conservator and is currently the Head of Education at this institute. As a conservation educator and researcher, she supervises and teaches conservation students enrolled in the University of Amsterdam programme and is involved in a number of research projects. She holds the role of Coordinator (2014-2017) for ICOM-CC Working Group 'Education and Training in Conservation'.

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Bianca van Velzen finished the post academic training program *Conservation of Paintings and Painted Objects* at the Stichting Restauratie Atelier Limburg in Maastricht in 2000. First she worked as a private conservator and joined the SRAL as staff conservator in 2006. Her special interests lie in the specific characteristics and potential problems of pictorial layers in relation to different types of supports such as Gilt Leather.

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APPENDICES

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Detail of the gilt leather panel, depicting the four seasons (Northern Netherlands, 1640-1660) Collection Deutsches Ledermuseum/ Schuhmuseum Offenbach, inv.no. 2572.