OR 42/2010

Norsk institutt for luftforskning
Norwegian Institute for Air Research

SIXTH FRAMEWORK PROGRAMME

PROPAINT

Improved Protection of Paintings during Exhibition, Storage and Transit
Final Activity Report

Elin Dahlin (ed.)

EU FP6 Supported Research Project:
SSPI-044254

Norwegian Institute for Air Research
Birkbeck University of London
Tate
Royal Danish Academy of Fine Arts The School of Conservation
Statens Museum for Kunst
SIT Transportes Internacionales
Fraunhofer Institut für Silicatforschung
National Museum in Krakow
University of Pisa

PROPAINT

Improved Protection of Paintings during Exhibition, Storage and Transit

Final Activity Report

Edited by

Elin Dahlin
Norwegian Institute for Air Research

PROPAINT is an EU research project funded through the Sixth Framework Programme, Scientific Support to Policies. The authors gratefully acknowledge the support by the European Commission, Directorate General “Research”, Directorate “Environment”, and from the Norwegian Archive, Library and Museum Authority.
The content of this publication relies on the sole responsibility of its authors.

List of contributors:

Elin Dahlin, Terje Grøntoft, Susana López-Aparicio
Norwegian Institute for Air Research (NILU), P.O.box 100, NO-2027 Kjeller, Norway.

Marianne Odlyha
Birkbeck College, Malet St. Bloomsbury, London WC1E 7HX, UK.

Mikkel Scharff, Tanja Larsen
Royal Danish Academy of Fine Arts, School of Conservation, (RDAFA.SC), Esplanaden 34, DK 1263 Copenhagen K, Denmark.

Guillermo Andrade, Ana Tabuenca García, Antonio Ortega
SIT Transportes Internacionales S.L., Avda. Fuentemar, 13, 28823 Coslada, Madrid, Spain.

Peter Mottner
Fraunhofer Institute for Silicate Research (ISC), Bronnbach Branch,
D-97877 Wertheim, Germany.

Michal Obarzanowski, Janusz Czop, Roman Kozłowski
National Museum in Kraków, al. 3 Maja 1, 30-062 Kraków, Poland.

Maria Perla Colombini, Ilaria Bonaduce
Dipartimento di Chimica e Chimica Industriale, Università di Pisa,
via Risorgimento 35, 56126 Pisa, Italy.

David Thickett
English Heritage, 1 Waterhouse Square, 138 Holborn, London EC1N 2ST, UK.

Stephen Hackney
Tate, Tate Britain, Millbank, London SW1P, 4RG, UK.

Jørgen Wadum, Anne Haack Christensen
Statens Museum for Kunst (SMK), Sølvgade 48-50, DK-1307 Copenhagen K, Denmark.

Morten Ryhl-Svendsen
National Museum of Denmark, Department of Conservation, IC Modewegsvej, Brede, DK-2800 Kgs. Lyngby, Denmark.

Sławomir Jakieła
Institute of Physical Chemistry, Polish Academy of Sciences, 44/52 Kasprzaka,
01-224 Warsaw, Poland.

Table of Contents

Preface

The content of this report is based on the results achieved during the EU funded project "Improved Protection of Paintings during Exhibition, Storage and Transit" – PROPAINT.
The PROPAINT project (SSPI – 044254) is a Specific Targeted Research Project (STREP) within the Thematic Area 8.1. Policy Oriented Research: Scientific Support to Policies, in the 6th Framework Programme. The duration of the project was three years from 1st February 2007 to 31st January 2010.

The research in PROPAINT was performed by a project consortium representing seven European Countries in close cooperation with an end-user group.

This final activity resport is the result of the scientific work from all the contributors in the PROPAINT project, and it describes the methodologies and approaches employed in order to reach the project objectives and relate the achievements of the project to the state of the art.

In order to make this publication more suitable for end-users and stakeholders the main chapters of the report starts with a summary followed by a sub-chapter explaining the implications of the PROPAINT results for preventive conservation of paintings. Each main chapter then presents more detailed and technical description of the methods, results and interpretations. This structure should make the report more useful both for general readers and experts.

More information about the project is available at the project web-site:
http://propaint.nilu.no

Elin Dahlin

Summary

The EU PROPAINT project (SSPI – 044254) was performed in the period 2007 – 2010. The project was co-ordinated by the Norwegian Institute for Air Research (NILU) and included seven partners, three subcontractors and 10 end-user museums. The rationale for the research in PROPAINT was to advance the state of the art in the use of microclimate frames for preventive conservation for paintings and contribute to better standards for microclimate control of paintings on display, in storage, and in transit.

Environmental measurements inside and outside of microclimate frames performed in 12 museum and one workshop location have shown the critical importance of the physical properties of the microclimate frames (i.e. the air exchange and volume). Concentrations of pollutants that infiltrate into the microclimate frame from outside (e.g. the oxidizing pollutants NO_2 and O_3, and SO_2) are usually very low, whereas concentrations of organic pollutants (e.g. acetic and formic acids, VOCs), which are emitted from materials enclosed by the frames, are typically higher than outside the frames. A concern was raised about the potential hazard to the paintings due to these compounds. It is known that the inorganic pollutants have diverse degradation effects on a range of organic and inorganic materials. Acetic acid is known to be aggressive to a range of mostly inorganic materials, but little is known about its possible degradation effect on the varnished surfaces of paintings.

PROPAINT has developed an environmental dosimetry system for evaluation of the impact on paintings in microclimate frames, which is now available to stakeholders responsible for the preservation of paintings. The system combines two dosimeters, one that measures photo-oxidizing impact and one that measures acidic impact. The system gives a more complete evaluation of the pollutant risk inside the microclimate frames. A "tolerance–location diagram" was developed for the interpretation of the dosimeter results. In the diagram the result for the measured environment is compared with the expected tolerable environment of cultural heritage locations with different degree of protection. For the piezoelectric quartz crystal dosimeters used in PROPAINT further miniaturisation and the development of a continuous recording module was made to enable real time monitoring within the frames.

PROPAINT describes the important properties of microclimate frames for preventive conservation based on the research performed and the experiences of the partners. Based on the measurement results and the performed modelling, it was shown that air tight frames (low ventilation rate) with low volume and as low as possible internal pollutant emissions will give the lowest pollutant dose to the paintings. In PROPAINT a decision making model for the construction of microclimate frames was developed. The model systematically goes through the steps in the production process of a microclimate frame and the main concerns related to preventive conservation properties of the microclimate frames.

An important part of PROPAINT was the work performed to understand the degradation of varnishes due to air pollutants. Varnishes were studied in PROPAINT as they are commonly the major surface of a painting meant to be viewed and in contact with the atmosphere. Damage to the varnish means that the underlying paint layer is more susceptible to damage, and eventually the painting may need re-varnishing interventions which pose an additional risk to the painting.

The research in PROPAINT showed that natural varnishes after their application and initial curing undergo rapid oxidation and cross linking. The rate of the oxidation and cross linking,

which produces a more brittle and less soluble varnish, was shown to depend on the pollutant doses (NO_2, O_3, acetic acid) both in laboratory exposures and in field exposures. It was found that the inclusion of the stabiliser Tinuvin 292 in dammar retarded the oxidation and cross linking processes, both under artificial and natural ageing. The investigated synthetic resins (i.e. MS2A, with and without Tinuvin 292, and Paraloid B72) showed little change under the ageing conditions compared to natural resins. Nevertheless both synthetic resins showed physic-chemical changes under natural and artificial ageing. Moreover it was shown that aromatic solvents used in the application of MS2A were trapped for a very long time in the varnish layer. The aromatic compounds are known to be dangerous to human health and may also be harmful for paint layers, as they could migrate towards the paint films and act as solvents for some of the paint constituents. This could affect the stability of paint layers, and contribute to the well known phenomenon of ghost images.

1 Introduction

1.1 Problems to be solved

Paintings are among the most important and most visited masterpieces in European museums, galleries and exhibition facilities. A main task for museum administrators and conservators is to preserve the paintings as close as possible to the artists' original expression. An important part of this work is the protection of paintings against degrading influences of the various indoor environments. Specially designed microclimate frames are increasingly being used for this purpose. There is a growing concern about the nature of the microclimate which develops over time inside these enclosed spaces and its potential to damage the paintings.

Scientific Objectives and Approach

The main aim of the PROPAINT project is:

To provide conservation staff and stakeholders with innovative protection treatments used as a preventive conservation measure for paintings during exhibition, storage and transit.

To achieve this aim, the following objectives were investigated:

- Evaluation of the protective effect of microclimate frames for paintings.
- Evaluation of the physical-chemical state and hence the protective effect of varnishes on paintings generally and in microclimate frames specifically.
- Contribution to preventive conservation strategies and standards for microclimate control of paintings on display, in storage and in transit.
- Optimisation of microclimate control and its implication for design of new microclimate enclosures.

How the objectives were met?

The environmental conditions inside microclimate frames, particularly the synergistic action of pollutants, humidity, temperature and light, had up to PROPAINT not been much investigated. One of the main objectives of PROPAINT was therefore to study the expected impact of pollutants and climate on paintings installed in microclimate frames by using different dosimeters. In addition, the protective effect of varnishes on paintings generally, and in microclimate frames specifically, were analysed and evaluated.

The current approach to the use of microclimate frames was reviewed in the very early stage of the project through consultation with end-users in a workshop. Information from this process enabled the design of both a laboratory and a field test programme for the evaluation of the combined impact of pollutants and climate on paintings installed in microclimate frames.

Early warning dosimeters developed in three previous EU funded projects (AMECP (EV5V-CT92-0144), MASTER (EVK4-CT-2002-00093) and MIMIC (EVKV-CT-2000-00040)) were used to assess the degradation effect on paintings, with and without varnish. In addition, certain selected gaseous pollutants were measured with appropriate gas sampling techniques. The results from the microclimate frames and varnish studies were used to develop remediation guidelines for stakeholders, and contributed to the work with the standard: CEN/TC 346/WG 4 N193 "Conservation of cultural heritage - Guidelines for management of

environmental conditions - Recommendations for showcases used for exhibition and preservation of cultural heritage". A microclimate frame can be seen as a particular showcase design, and the control of the microclimate for paintings by the use of microclimate frames is addressed by this standard.

PROPAINT has fulfilled the objectives to a state where the systems for environmental dosimetry and related methods for environmental impact evaluation for paintings in microclimate frames are available to users responsible for the preservation of paintings.
Further a better understanding of the protective effect of varnish remediation treatments for paintings has been achieved. New and better design for microclimate frames has been developed in close cooperation with the end-users and their needs.

Contractors involved in PROPAINT were:

CO1-NILU Norwegian Institute for Air Research P.O. Box 100, NO-2027 Kjeller, Norway	**Elin Dahlin** emd@nilu.no Phone: + 47 63 89 80 00 Fax: + 47 63 89 80 50
CR2-BIRKBECK BIRKBECK College, Department of Chemistry, University of London Malet St. Bloomsbury, London WC1E 7HX, UK	**Marianne Odlyha** m.odlyha@bbk.ac.uk Phone: + 44 (0) 20 70 79 07 92 Fax: + 44 (0) 20 70 79 07 92
CR 4-RDAFA.SC Royal Danish Academy of Fine Arts, The School of Conservation Esplanaden 34, DK 1263 Copenhagen K, Denmark	**Mikkel Scharff** ms@kons.dk Phone: + 45 33 74 47 60 Fax: +45 3374 47 77
CR 5-Artyd SIT – International Transporters Avda. Fuentemar, 13, ES-28820 Coslada, Madrid, Spain	**Guillermo Andrade** artyd.info@gmail.com Phone: + 34 91 67 10 608 Fax: + 34 91 674 0654
CR 6-ISC Fraunhofer Institute for Silicate Research Bronnbach Branch, DE-97877 Wertheim-Bronnbach, Germany	**Peter Mottner** mottner@isc.fraunhofer.de Phone: + 49 (0)9342 9221 711 (-701) Fax. +49 (0)9342 9221 799
CR 7-MNK National Museum in Krakow Al. 3 Maja 1, 30-062 Krakow, Poland	**Janusz Czop** jczop@muzeum.krakow.pl Phone: + 48 12 295 55 80 Fax: + 48 12 63 39 767
CR 8-DCCI Department of Chemistry and Industrial Chemistry, University of Pisa Via Risorgimento 35, IT-56126 Pisa, Italy	**Maria Perla Colombini** perla@dcci.unipi.it Phone: + 39 050 22 19 305/ + 39 338 59 44 223 Fax: + 39 050 2219260

Coordinator contact details:
Name: Elin Dahlin
Postal address: P.O. Box 100, NO-2027 Kjeller, Norway
Visiting address: Instituttveien 18, NO-2027 Kjeller, Norway
Phone: + 47 63 89 80 00 Fax: + 47 63 89 80 50
E-mail: emd@nilu.no Website: www.nilu.no

Subcontractors were:

- Tate, London (Tate), UK. Contact person: Stephen Hackney,
- QuartzTec (QT), UK. Contact persons: Mark Appleton and J. M. Slater
- Statens Museum for Kunst (SMK), DK. Contact person: Jørgen Wadum

End-users were:

Institution	**Contact person**	**Position**
Nasjonalmuseet for Kunst, Arkitektur og Design, Oslo, Norway	Trond E. Aslaksby	Conservator
National Museum in Krakow, Poland	Janusz Czop	Head Conservator
Tate, London, UK	Stephen Hackney	Manager, Conservation Science
National Art Museum, Mexico City**,** Mexico	Elizabeth Herrera Cisneros	Conservator
English Heritage, London, UK	David Thickett	Senior Conservation Scientist
Germanishes Nationalmuseum, Nürnberg, Germany	Arnulf von Ulmann	Head of the Institute of Art Techniques and Conservation
Statens Museum for Kunst, Copenhagen, Denmark	Jørgen Wadum	Keeper of Conservation
Fine Arts Museum, Valencia, Spain	Pilar Ineba	Conservator
Uffizi Gallery, Florence, Italy	Francesca de Luca	Curator
Centre for Conservation Science, and Restoration Techniques, National Research Institute of Cultural Properties, Tokyo, Japan	Takeshi Ishizaki	Director

2 Background knowledge

The work in PROPAINT was performed based on the present knowledge about microclimate frames for paintings and their historical use. The development of the state of the art was further based on detailed background knowledge about varnish protection of paintings and varnish degradation. In addition background knowledge about air pollution measurement techniques and evaluation of environmental quality for cultural heritage were used. This section synthesizes the background knowledge in these fields as the starting point for the description of PROPAINT work, results and development of the state of the art.

2.1 Use of microclimate frames for paintings

Introduction

Paintings have a multi-layered heterogeneous structure: the individual paint layers, which contain a combination of several pigments held in the binder, are supported on a glue-sized and primed canvas. Wood and canvas were the two main historical supports to create panel and canvas–supported paintings where the canvas was held taut using wooden stretcher bars. Glue size layers differed in type and amount of size used, as well as in the application techniques. The ground layers most commonly were constituted of animal glue mixed with gypsum. Depending on the painting technique a priming layer could be present, where a binder (proteinaceous or oily mostly) mixed with a pigment/dryer was applied on top of the ground layer. In addition, varnishes differed in the type of resin used (Gettens and Stout, 1966; Mills, 1999).

The effects of a wide range of deterioration phenomena due to natural ageing, impact of environmental hazards, and past conservation and/or restoration treatments add to the complexity of the problems posed for characterising the materials. The conservation of the paintings has evolved from early craftsmanship based on subjective and intuitive criteria into a modern specialised profession based on conservation science including chemical and physical analyses of the paintings.

The development of preventive conservation since 1980s has been particularly important. However, the use of microclimate boxes or frames to protect vulnerable paintings is not just a new phenomenon from the recent few decades. The upward trend in the circulation of travelling exhibitions in recent years has increased the need to protect paintings during these periods. This survey, primarily based on Wadum (1998) lists the main developments in the use and design of microclimate frames since 1892. They vary according to different principles and may be divided into three broad groups:

- Frames with an active buffer material to stabilize the internal relative humidity
- Frames containing no added buffer material (but well sealed)
- Frames with an altered atmospheric content.

Early microclimate frames

The first known attempt to make a microclimate frame was in England in 1892 (Simpson, 1893). It was done for a painting, Venice from the Canale della Guidecca di Santa Maria della Salute, by J.M.W. Turner in the Victoria & Albert Museum. The characterization of the sealed, air tight slender box which was tailored to fit the specific painting is very similar to a modern microclimate frame. Simpsons frame was even meant to fit into the original gilt frame, and to be hung in the usual manner. The front would be glass and the back of glass, metal or other material. In Simpsons frame, nozzles were placed at the bottom for attachment

to an exhauster to extract air from the box in order to create a vacuum around the picture. Although the long term integrity of the vacuum has been questioned, Simpson's frame was in fact the first approach to create an altered gaseous content around the object enclosed in the microenvironment. The frame has not been opened to this day and the opinion is that the painting, which was enclosed because it was in poor condition, is nowadays in better condition than its unprotected contemporaries.

With the article "*A Micro-micro-climate"* published by Diamond (1974) came the first description of a microclimate frame for a panel painting on display, based on the studies of Thomson (1961, 1964) and Stolow (1965, 1967). A sixteenth century French portrait from the school of François Clouet, was placed in a showcase. Accordingly a box of hardwood with chipboard back was constructed, fitted at the front with glass which was puttied in to make an airtight seal.

Toishi & Miura (1977) and Miura (1978) described how the Mona Lisa from the Louvre was exhibited for fifty days in the Tokyo National Museum. During this exhibition the painting was enclosed in an iron case lined with a 75 mm glass layer and having a double panel glass window. In order to maintain a stable relative humidity of 50% zeolite was enclosed into the case. The zeolite was found to be capable of absorbing various gasses such as sulphur dioxide, hydrogen sulphide, ammonia, carbon dioxide and formaldehyde (Kenjo and Toishi 1975).

The use of microclimate frames with an active buffer material

The classic contribution concerning the phenomena on controlling microclimates (Thomson 1977) states that for relative humidity (RH) conditions above 50% silica gel offers little advantage over wood, its M-value (moisture gain in g/kg for a 1% RH rise) being about the same, but at lower RH values silica gel is the best buffer. The leakage rate for the case is important, and he refers to the important studies by Padfield (1966) on the problem of diffusion through materials of various kinds.

An example of the use of humidity buffers in microclimate frames was the framing of Tate Panels in the Church of All Hallows Berkyngechirche by the Tower, as described by Knight (1983). A box was made of Perspex, with a sheet of aluminium as backing board. Steel angle iron brackets made the attachment to the wall, thus leaving an air gap between the back plate and the wall. Based on the recommendations of Stolow (1967) and Sack and Stolow (1978) the humidity control of the box was carried out by placing silica gel in small narrow trays which could be individually removed for re-conditioning. Evidence of the protection against external pollution afforded to canvas by glazing was provided by Hackney and Hedley (1984) and museums began to incorporate backboards and glazing systematically to framed oil paintings (Hackney 1990).

Contrary to the use of large microclimate enclosures encapsulating picture and frame, Cassar (1988) and Edmunds (1988) individually presented microclimate frames designed to fit within the frame of the painting (also described previously by Ramer, 1984). Bosshard and Richard (1989) recognized the disadvantage of a microclimate frame that enclosed a painting and its frame.

In the Mauritshuis museum (The Netherlands) a microclimate frame was constructed in 1990 to be fitted within the frame (Wadum, 1992), largely following the concepts of Ramer (1984), Bosshard (1990) and Edmunds (1988). The glazing was, however, always a layered safety glass enabling the frame to travel with minimum risk. At first silica gel or Art-sorb sheets was

included into the microclimate frame to stabilize the RH within the frame during display and transit.

Simultaneously with the Mauritshuis, the Rijksmuseum developed a microclimate frame. This box, being a low-budget variant, was initiated and constructed by Sozzani (1992). It consisted of a safety glass mounted and sealed in the rebate of the frame. Behind this the painting was mounted in the usual way. Thin wooden battens as a build up on the back of the frame gave enough depth in the rebate to enable the back cover of stainless steel to also carry a sheet of Art-sorb, before being closed on air-tight gaskets.

Extensive studies undertaken by Richard (1994) have confirmed that temperature changes affect panel paintings much faster than relative humidity variations. Despite his conclusion that silica gel indeed does not have any effect on the temperature changes, he recommended to keep it inside the microclimate frames. His assumption is based on the fact that virtually all microclimate frames leak, and therefore silica gel would play an important role in stabilizing the RH in cases displayed for a long period of time in an unsuitable environment.

Microclimate frames containing no added buffer material

Proposals have been made to rely on the hygroscopic behaviour of the wood panel itself as a stabilizing factor within a small air volume, when constructing microclimate frames. These frames were not kept at a stable RH by added buffers, but maintained their own internal moisture equilibrium at changing temperature by the hygroscopic capacity of the frame and artwork itself.

A critical approach to the consistent recommendation on the use of a moisture buffer in small display cases was presented by Ashley-Smith and Moncrieff (1984). Their experiences in the Victoria & Albert Museum (London) showed that the silica gel in a showcase does take away the short time fluctuations of RH, but the seasonal changes were not made up for. The poor results from the use of silica gel in showcases made of wood indicate that its use does not compensate the associated disadvantages such as time and expenses. An ordinary wooden showcase, without silica gel, performed nearly as well (or badly) in reducing short time humidity fluctuations. In addition Hackney (1987) warned against enclosing buffering materials such as silica gel in small sealed environments and underlined, as authors before him (Stolow, 1965; Stolow, 1967; Thomson, 1964; Thomson, 1977; Weintraub, 1982) that silica gel or similar buffers were not dependent on changes in temperature, but always remained in equilibrium at any temperature. Hygroscopic materials such as wood on the contrary stayed in equilibrium with high RH at high temperatures and vice versa.

Some of the most recent microclimate frames for panel paintings are now made without any added sorbent material. The buffering role of the panel itself is regarded sufficient in the small enclosed environment within a microclimate frame. Much care is, however, taken to ensure stable temperatures around the microclimate frame, this being on display in the gallery or in transport (Wadum, 1993). Thermal insulated transit crates may on long journeys maintain a relatively stable temperature inside the microclimate frame (Wadum, 1993).

Microclimate frames with an altered atmospheric content

Apart from the very early attempt of the 1890s only the recent twenty years have shown an increasing interest in the use of microclimate frames with an altered gaseous content. These microclimate frames are mainly made in order to reduce the deteriorating effects of oxygen. Low and close to zero oxygen content can be obtained by purging with N_2 and by the use of

oxygen scavengers. The use of oxygen scavengers (e.g. Ageless®) as a means of generating low oxygen atmospheres for the treatment of insect infested museum objects is discussed by Gilberg (1990). Ageless® is a type of oxygen scavenger, which is described by manufacturer to be a mixture of finely divided moist iron (ferrous) oxide and potassium chloride, which rapidly absorbs atmospheric oxygen. Further investigations on the reactions and usefulness of Ageless® were undertaken at the Getty Conservation Institute (GCI) in order to develop hermetically sealed inert gas-filled display and storage cases (Lambert et al., 1982). More recently, a study of anoxia applied to the framing and display of light-sensitive museum objects and works of art on paper has been carried out at Tate.

Recent literature

Since the review of Wadum (1993), the monitoring and control of microclimates for preventive conservation have received an ever increasing attention in literature. Especially the effects of material emission inside microenvironments (Oosten, 2002; Hatchfield, 2002; Tétreault, 2003), and the monitoring and quantification of the air quality herein (Dahlin et al., 2005; Godoi et al., 2004; Hahn et al., 2007; Odlyha et al., 2005a and 2005b; Odlyha et al., 2007; Ryhl-Svendsen, 2006; Ryhl-Svendsen, 2008; Schieweck et al., 2007a; Schieweck et al., 2007b; Wise et al., 2005) are explored in the recent literature, combined with a number of case studies and descriptions of climate within microclimate frames or display cases (Blow et al., 2003; Boddi et al., 1999; Dohety et al., 2008; Holmberg and Kippes, 2002; Toledo et al., 2007).

The control of air exchange, and the importance of relative humidity control either by the sealing of microclimate enclosures and/or by adding extra buffer material is another key issue (Boddi et al., 1999; Camuffo et al., 2000; Dohety et al., 2008; Holmberg and Kippes, 2003; Kampa, 2000; Knop et al., 2007; Maish et al., 1999; McPail et al., 2003; Norton et al., 2006; Padfield et al., 2002; Richards, 2007; Svare and Lyng Petersen, 2000; Thickett, 2005; Thickett et al., 2005; Thickett et al., 2007; Wadum, 2000; Weintraub, 2002; Yu et al., 2001). Modified atmospheres (Carrió and Stevenson, 2003; Maekawa, 1998), as well as the control of internally generated pollutants in confined enclosures (Newnham, 2002; Cruz et al, 2008) does receive some attention. However, no new innovative design has been added to the already mentioned basic types of microclimate frames (i.e. frames with an active buffer material to stabilize the internal RH, frames containing no added buffer material and well sealed, frames with an altered atmospheric content).

From published articles found on topics related and relevant to the PROPAINT agenda in the period 1995 - 2009, a brief classification was made and sorted according to their relevance and subject (Table 1).

Table 1: Recent literature related to microclimate frames.

Literature's relevance to:	**Reference**
Construction of microclimate frames	Knop et al., 2007 Richards, 2007 Wise et al., 2005 McPail et al., 2003 Wadum, 2000
Use of microclimate frames	Thickett et al., 2007 Dohety et al., 2008 Richards, 2007 Toledo et al., 2007 Norton and Furuhata, 2006 Thickett, 2005 Thickett et al., 2005 Bülow et al., 2003 Padfield et al., 2002 Bacon and Martin, 2000 Svare et al., 2000 Wadum, 2000 Di Pietro and Ligterink, 1999a Maish et al., 1999
Monitoring and modelling of microclimates (in general)	Cruz et al., 2008 Ryhl-Svendsen, 2008 Thickett et al., 2007 Watts et al., 2007 Ryhl-Svendsen, 2006 Dahlin et al., 2005 Odlyha, et al, 2005a Tétreault, 2003b Odlyha, et al., 2000 Wadum, 2000
Degradation parameters and materials research (in microclimates)	Mecklenburg, 2007 Hahn et al., 2007 Schieweck et al., 2007a Schieweck et al., 2007b Carrió and Stevenson, 2003 Tétreault, 2003a Tétreault, 2003b Hatchfield, 2002
General issues regarding microclimates	Shiner, 2007 Watts et al., 2007 Tétreault, 2003b Hatchfield, 2002 Camuffo, 2000 Camuffo et al., 2000

2.2 Varnishes

Natural plant resins have been used since ancient times for a wide range of applications: varnishes, sealant, binding media and waterproofing. Transparent coatings on easel paintings fulfil aesthetic functions, saturate the colours and give gloss to the paintings. Moreover, the varnish layer protects the paint film from dirt, environmental influences and mechanical damage.

Historically, paint varnishes have been described by Theophilus in the 11th century and Cennino Cennini in the 15th century, who reported various recipes such as oil varnishes obtained by dissolving natural resins, such as sandarac, rosin or mastic, in drying oils (oilseed or walnut oil).

Later on, from the 16th century, spirit varnishes became more common. These were solutions of natural resins in a volatile solvent, usually oil of turpentine dissolved in turpentine or in natural naphtha, and later in alcohol. Recipes used by Flemish painters describe Venice turpentine dissolved in spirits of turpentine, with occasional addition of sandarac, mastic, and plant oils. Triterpenoid resins such as mastic and dammar, which was introduced in Europe only in the 19th century, were the most popular varnishes. Artists and restorers preferentially used triterpenoid resins because of their excellent adhesive properties, their good solubility in solvents and because they yellow to a lesser extent than varnishes made with diterpenoid resins (de la Rie, 1987).

Plant resins are lipid-soluble mixtures of volatile and non-volatile terpenoid and/or phenolic secondary compounds that are usually secreted in specialized structures located either internally or on the surface of the plant. Natural resins are substances with a high viscosity, semisolids or solid and insoluble in water. They are formed in the so-called “resiniferous canals” of several trees. Many varieties of plants spontaneously exude resins as a product of their metabolism, to protect themselves against excessive loss of water and attacks by micro-organisms (Colombini and Modugno, 2009).

From a chemical point of view, plant resins are a complex mixture of mono-, sesqui-, di- and triterpenes, which have 10, 15, 20, and 30 carbon atoms per molecule, respectively. The mono- and sesquiterpenes are both present in most resins. The di- and triterpenes are rarely found together in the same resin, which means that terpenic resins can be divided into two main classes, diterpenoid and triterpenoid resins. Table 2 lists the botanical origin and the kind of terpenoid compounds of some natural resins.

Table 2: Botanical origin and chemical composition of terpenic resins (Colombini and Modugno, 2009).

Plant resins			
Class	**Family**	**Genus (type of resin)**	**Composition**
Coniferales	**Pinaceae**	*Pinus* (pine resin, colophony)	abietadienic acids pimaradienic acids
		Abies (Strasbourg turpentine)	abietadienic acids pimaradienic acids cis-abienol
		Larix (Venice turpentine)	abietadienic acids pimaradienic acids epimanool, larixol, larixyl acetate
	Cupressaceae	J*uniper*, *Cupressus*, *Tetraclinis articulata* (sandarac)	pimaradienic acids (sandaracopimaric acid), communic acid, totarol
Guttiferales	**Dipterocarpaceae**	*Hopea* (dammar)	dammaranes (hydroxydammarenone, dammaradienol), ursanes (ursonic acid, ursonaldehyde)
Terebinthales	**Anacardiaceae**	*Pistacia* (mastic)	euphanes (masticadienonic acid, isomasticadienonic acid), oleanananes (oleanonic acid, moronic acid), dammaranes
	Burseraceae	*Commiphora* (myrrh)	α and β- amyrin euphanes oleananes
		Boswellia (olibanum or frankincense)	
		Canarium (elemi)	

The triterpenoid mastic and dammar are still used today as varnishes. Particularly, dammar resin seems the most used one for its good optical properties and low acidity. Actually, dammar mixed with solvents became the preferred varnish for oil painting, due to superior optical properties and better ageing stability than the other natural resins.

Mastic resin of Pistacia lentiscus L. (Anacardiaceae) consists of triterpenoids together with a smaller proportion of polymeric material known as poly-β- myrcene.

Dammar resin originates from trees of the Dipterocarpaceae family, which grow in the East Indies. The trees exude sticky by-products of their metabolism, which yield the resin after the volatile components have evaporated. The primary constituents are triterpenoids, and a small polymeric fraction, known as polycadinene, is also present. Some characteristic compounds allow the identification of the botanical origin of the resin (Mills and White, 1999).

The ageing of triterpenoid compounds has been extensively studied, and interesting results have been achieved by artificially ageing of triterpenoid resins with UV light, as well as natural ageing under light and dark conditions. An extensive knowledge of the resin chemical composition, in terms of original components and oxidation products is available (Dietemann et al., 2000, 2003, 2005; Scalarone 2005; van der Doelen 2000; Theodorakopoulos, 2009). Up to now there have been only a few studies at the molecular level of the effects of atmospheric pollutants on these varnishes (West et al., 2004), and further research is therefore required.

Molecular markers can, thus, be used to recognize terpenoid resins in old samples and to distinguish between mastic and dammar resins (Colombini and Tassi, 2008). Based on studies on artificially and naturally aged resins, the most abundant compounds that can be used as markers for identifying the mastic resin are oleanonic acid, 20,24-epoxy-25-hydroxy-dammaran-3-one, and moronic acid. For dammar resin, dammarenolic acid, 20,24-epoxy-25-hydroxy-dammaran-3-one,20,24-epoxy-25-hydroxy-dammaran-3-ol, hydroxydammarenone, dihydro-dammarenolic acid, 3,4-seco-urs-12-en-3,28-dioic acid and shoreic and eichlerianico can be used.

The molecular weight distribution of dammar films changes during ageing because most of the free triterpenoid fraction disappears during light ageing, and material of higher molecular weight is formed. During ageing, absorption in the UV range increases and also occurs at increasingly longer wavelengths. Consequently, yellowing occurs and absorptions appear in the short-wavelength visible range of the light spectrum. Hazing and cracking cause a general decrease in transmission (increase in scattering). This aspect clearly shows up in the long-wavelength part of the visible range of the spectrum, where no absorption occurs. The data indicate that photochemically initiated autoxidation is followed by non-oxidative thermal reactions, which cause yellowing. The triterpenoid fraction of dammar resin contains tetracyclic and pentacyclic compounds that have keto, ether, tertiary carbon, and olefinic functions. These groups are all susceptible to photochemically initiated radical reactions. The change in solubility is clearly caused by the formation of more polar oxidation products, particularly those containing carboxylic acid groups (de la Rie, 1989).

Aging and exposure to light profoundly change the composition of an oxidized resin species and high molecular weight material are produced due to condensation and light-induced radical reactions. These transformations, which depend on the exposure time, wavelength of light and thickness of the resin layer, give the varnish a yellowish colour. Indeed, the darkening and the yellowing of terpenoid varnish films due to ageing is one of the main conservation problems in paintings, and periodically the varnish film needs to be removed and replaced with a new one. The oxidized terpenoid films are soluble only in polar solvents, which may also affect the paint layer (Dietemann, 2003).

There are several hypotheses regarding the yellowing of triterpenoid varnishes. According to de la Rie (1989), yellowing may be related to the occurrence of dehydration and condensation. Dietemann et al. (2000) suggest that this phenomenon is caused by a general breakdown of the initial compounds. Finally, van der Doelen et al. (2000) suggest that the yellow colour of aged dammar is caused by the formation of a relatively high molecular weight material.

The introduction of synthetic paints, starting from nitrocellulose (pyroxylin) lacquers, made available to the twentieth century artists a wide range of new materials which they have used as binding media, coatings and adhesives. Many types of synthetic varnishes were introduced,

mostly composed of ketone or acrylic resins dissolved in mineral spirits (Colombini and Modugno, 2009).

Advantages of such varnishes are their inherent higher stability compared to those based on natural resins. On the other hand synthetic polymers may show poorer optical characteristics, and this has been attributed to the higher solution viscosities brought by the high molecular weights of the polymers involved. In particular:

- Acrylic and methacrylic resins have been employed due to resistance to yellowing at room temperature (Osete-Cortina and Domenech-Carbò, 2006). Low values of glass transition temperature bring, with time, to the uptake of particulates in the coating layer, with loss of transparency and gloss. Among the more widely used acrylic polymers is Paraloid B72, a ethyl-methacrylate copolymer which shows low tendency to cross linking with ageing and remains quite soluble (Chiantore et al., 2000; Lazzari and Chiantore, 2000). However, acrylic coatings change the appearance of a painting as gloss and colour saturation are reduced in comparison with traditional resin varnishes due to the increased light scattering at the surface;

- Low molecular weight (LMW) synthetic resins are able to mimic natural resins better than the acrylic ones. Ketone or polycyclohexanone resins (AW2 by BASF, MS2 by Laport Industries, Ketone Resin N by BASF, Laropal K80 by BASF), generally sold as additives to improve the gloss and hardness of industrial paints and coatings, were used to varnish paintings since the 1950s. Reduced ketone resins (MS2A and MS2B by Laport Industries), in which the ketone group is reduced to hydroxyl, were introduced in the 1960s. They were more photochemically stable than ketone resins, but also more brittle because of the increased hydrogen bonding (de la Rie and Shedrinsky, 1989; Maines and de la Rie, 2005). Moreover, the addition of Tinuvin 292 has been suggested to improve the stability of varnishes by reducing radical reactions (Routledge, 2000). Tinuvin 292 is a liquid hindered amine light stabilizer especially developed for coatings.

However, we are not fully aware of the chemical and physical behaviour of modern synthetic materials and their characterization and conservation is very complex. This is particularly true concerning the interactions with the components in art objects, interactions with additives (e.g. fillers, plasticisers, colorants), and changes in their properties during ageing. Since synthetic polymers are commercial products, the materials used in the past may significantly differ from modern materials of nominally the same composition, thus hampering characterization and comparisons.

Old yellowed natural as well as synthetic varnishes are often removed with rather polar solvents, which can damage the painting by swelling and leaching of paint components. It is therefore desirable to deepen our understanding of the ageing behaviour of these resins for a better protection of valuable works of art.

2.3 Environmental measurements

2.3.1 Climate

"Climate" is the combined physical properties of the air-environment including factors such as temperature, humidity, atmospheric pressure, wind, rainfall, and numerous other meteorological elements at a location over long periods of time. The indoor climate can be defined in a similar way on a smaller scale, considering the protection effect of the building shell against the large scale outdoors. The main climate factors that are usually considered in preventive conservation of heritage objects indoors are temperature, humidity, air flow (ventilation) conditions, and light (including UV light). The degradation impact of these factors on the indoor cultural heritage objects have been given much attention and most museums, archives and libraries measure the temperature, relative humidity (RH) and light/UV conditions. More extensive climate measurements in a museum can give information about climate variation in space and time, which is useful when determining the location for individual objects such as paintings depending on their vulnerability. Such information can also tell about the climate functioning of the building, e.g. ventilation and air flow patterns and insulation properties.

The main focus of the PROPAINT project was the evaluation of pollutant impact in microclimate frames. Apart from the general description of climate control by microclimate frames given in Chapter 3.1, this report will not go into detail on the subject of climate control. The conservation literature recommends levels and maximum ranges of fluctuation in these parameters for preventive conservation of artefacts made from different materials. Generally, the recommended levels are around 50% RH, but with some variation depending on the material (e.g. metal and stone should be kept at lower humidity). The temperature should be stable and as low as practically possible to reduce degradation rates, but considering possible physical damage due to increased brittleness (Tétreault, 2003). It is recommended that objects are exposed to no UV and only sufficient low light for visitors to appreciate exhibited objects.

Considering, more particularly, the preservation of paintings it is important to know the environmental, including climate, conditions under which a painting is displayed or stored, whether in a microclimate frame or not. Paintings are not static structures and they respond to changes in RH and temperature, since they contain moisture sensitive materials such as canvas, wood and glue. A typical scenario for paintings in unstable climates is that the tension in the stretched canvas changes with the RH, whereas the oil paint is much less liable to respond dimensionally to moisture. The difference in response causes inter-laminar stress, potentially leading to de-lamination of paint layers. One of the purposes of microclimate frames is to minimize fluctuations in RH and, to some extent, temperature, which is why it is important to be able to monitor the climate inside the frames.

The climate in microclimate frames can be measured using data loggers to register temperature and relative humidity. Possible fluctuations in the two parameters can be recorded continuously and compared to the climate outside the frame, making it possible to assess the buffering properties of the microclimate frames over time. It is possible to acquire mechanical thermo hygrometers small enough to fit into a microclimate frame. However they do not, like the data loggers and the thermo hygrographs, record the fluctuations in the climate over time. In the PROPAINT project different types of data loggers have been used to record temperature and relative humidity.

Figure 1 and Figure 2 show the typical buffering of climate (T and RH) inside two microclimate frames studied in PROPAINT. One is a microclimate frame with low ventilation (0.39 d^{-1}) at the Statens Museum for Kunst (Figure 1; No. 8 in Table 3) and the second is the "Leonardo frame" with relatively high ventilation (15 d^{-1}) studied by the National Museum in Krakow (Figure 2; No. 12 in Table 3).

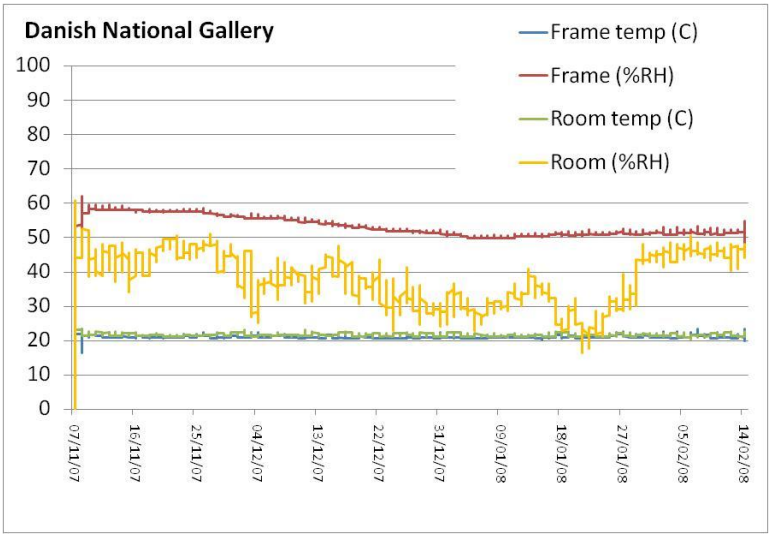


Figure 1: Temperature and relative humidity measured inside and outside of a microclimate frame at the Statens Museum for Kunst, Copenhagen, Denmark.

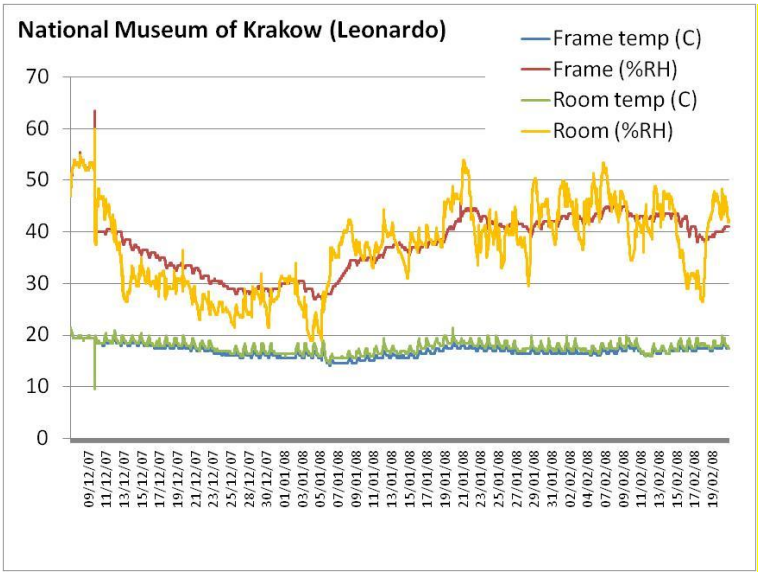


Figure 2: Temperature and relative humidity measured inside and outside the "Leonardo frame" by the National Museum in Krakow, Poland.

2.3.2 Pollutants

2.3.2.1 Introduction

Indoor air pollutants are gases and particles that deposit on and react with surfaces of cultural heritage objects and might change their properties and appearance and thus the artistic value of e.g. paintings. Gaseous pollutants that can degrade cultural heritage objects are present indoors in heritage buildings such as museums, libraries and archives (e.g. Grøntoft et al., 2005, Lopez-Aparicio et al., 2009). Measurement of indoor concentration levels of these pollutants and of their impact on cultural heritage objects is important. Based on such information preventive conservation strategies can be implemented to improve the environmental conditions and thus long term preservation of the objects.

2.3.2.2 Measurement methods

Environmental monitoring strategies used in preventive conservation can be divided into two main categories: parameter monitoring and dosimetry. The different measurement methods were developed since the mid 20th century. Parameter monitoring techniques were the first to be developed. In the few last decennia several methods for environmental dosimetry have been developed.

The most common method of environmental monitoring has been parameter monitoring, where scientific measurements are made on numerical scales of relevant parameters such as temperature, relative humidity, light and air pollution. Parameter monitoring of pollutant gases can today be performed with a large range of different types of instruments. Large and expensive monitors are available for continuous measurements of most types of air pollutants. It has been an aim in air pollution monitoring to produce smaller, less expensive instruments for accurate and sensitive continuous monitoring of single pollutants. Such instruments exist for a range of pollutants based on e.g. electrochemical principles. For most components their sensitivity is however too low to serve the needs of environmental measurements for cultural heritage purposes.

In the other end of the range of complexity and price is passive diffusion sampling. Passive diffusion gas samplers collect the pollutant over some time and the result is usually presented as an average concentration value. This measure also represents the time integrated pollutant dose and is often regarded as a good measure for the impact of the environment on cultural heritage objects - as opposed to the importance of peak values for impacts on health. A disadvantage is that the diffusion samplers cannot easily be used to diagnose sudden changes in the environment. For this other instrumental or dosimetry methods are needed. Passive diffusion samplers can also be used outdoors. For outdoor locations continuous values from instruments measurements at monitoring stations may however be available. Figure 3 shows some typical passive diffusion gas sampler designs.

The meaning of data from parameter monitoring for preventive conservation is interpreted using background knowledge from scientific studies of the interaction between materials and levels of the parameter, either through accelerated ageing tests (e.g. Zinn et al., 1994) or natural ageing in field tests (e.g. Larsen 1996). The latter method is much rarer than the former because of the long timescales of natural ageing and the difficulty in collecting historic data about exposure conditions throughout the lifetime of an object.

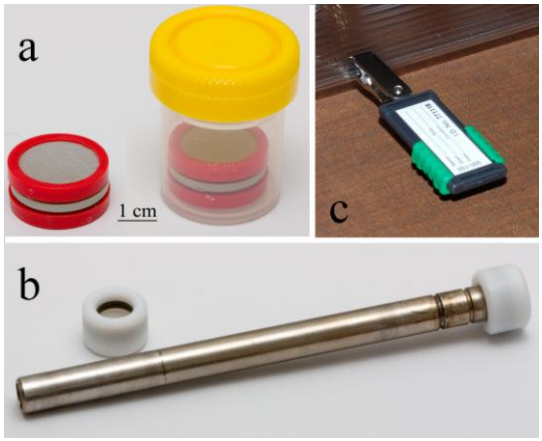


Figure 3: Examples of passive diffusion gas samplers for a) A range of gases depending on preparation of absorbing medium. b) Volatile Organic Compounds (VOCs) and c) Formaldehyde.

Dosimetry can be thought of as the inverse of parameter monitoring. In parameter monitoring the potential for deterioration is inferred from environmental measurement. We assume we are measuring all the relevant parameters and may have to employ a range of techniques to do so. In dosimetry some form of sacrificial material that responds similarly to the materials of interest is exposed to the environment, and from its deterioration, the quality of the environment is inferred. Dosimetry has the advantage that a generic and synergistic integrated effect of all or a part of the different environmental factors (parameters) present in the environment (e.g. climate, light, pollutants) is usually measured.

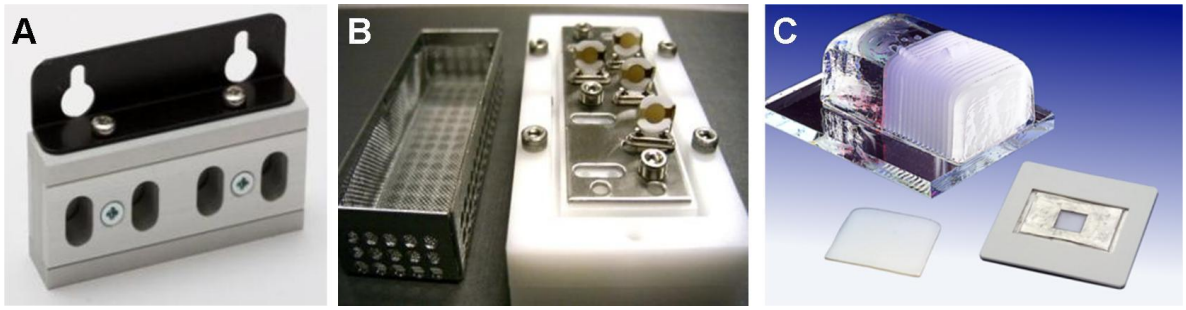


Figure 4: The main dosimeters used in the PROPAINT project: A. The NILU EWO (Early Warning dosimeter for Organic materials). B. The Birkbeck PQC (Piezoelectric Quartz Crystal) dosimeter and C. The Fraunhofer ISC GSD (Glass Slide Dosimeter).

In addition to the dosimeters used in PROPAINT (Figure 4, Chapter 5.3.2) other types of dosimeters such as the LightCheck© devices developed as part of the EC "LIDO" project (EVK4-CT-2000-00016), (Bacci et al., 2003), Blue Wool standards (Bullock and Saunders, 1999) and metal coupons made of lead, copper or silver (Oddy, 1973) can be mentioned. It is a characteristic of all these dosimeters that they are relatively easy to make and cheap to buy. On the simplest level their response is a visible change. They are often amenable to more

detailed analysis, if needed. For instance, the corrosion layers on metal coupons can be subject to electrochemical reduction and various spectroscopic analysis techniques, and the degree of light fading of a dye can either be compared with a card strip or quantified with a colour meter.

Some dosimeters respond greatly to one factor, e.g. light fading and for practical purposes can be considered as single parameter dosimeters, but will however also respond more subtly to other factors such as air pollution and temperature. For some dosimeters the responses are more evenly distributed. For instance, the corrosion of lead coupons requires organic acids and a sufficient degree of humidity. The reaction is probably further accelerated by temperature and the presence of other pollutants. This generic response is useful for a device that is intended to give an overall indication of environmental quality. It is less useful for diagnostic purposes where a problem has been found because of there is no clear indication of which parameter is causing the problem. In this case more diagnostic monitoring techniques would be needed to identify the specific cause(s) of the problem.

Dosimeters also need to respond more quickly than collection materials to the environment. Otherwise the information they give could have just as easily been obtained from examining the collections material itself. In the case of light dosimeters the response can be speeded up by using very light-sensitive dyes. For other materials such as silver coupons, it is less obvious how their response can be speeded up compared with a silver object. In practice this can be done by making sure the surface is clean, by scrubbing with an abrasive before exposure.

Thus, it is possible to relate the response of a dosimeter directly to the environment it is exposed in, and extrapolate from this what might happen to a material we wish to conserve, in that environment.

Background knowledge from both parameter monitoring and dosimetry underpins the formulation of standards and guidelines for preventive conservation. However, the data used are subject to many uncertainties such as those in extrapolating from accelerating ageing to what actually happens more slowly under ambient conditions. By contrast the methods used to measure environmental parameters are generally much more precise. It follows therefore that, at least in an early warning strategy; a semi-quantitative measure of environmental quality may well suffice. Therefore measurement by dosimetry may be entirely sufficient and has the advantages of often being easier and cheaper to carry out. The impact of environments on dosimeters can also be calibrated with simultaneous parameter measurements to get more information about the environmental impact and more information for comparison with impact on the cultural heritage materials and objects.

3 Measurements of environment for paintings

3.1 Summary

PROPAINT has developed a novel method for environmental dosimetry to be used for evaluation of indoor (including microclimate frame) air quality for cultural heritage locations. This new method is now available to stakeholders responsible for the preservation of paintings.

The system combines two dosimeters, one that measures photo-oxidizing impact and one that measures acidic impact. The system gives a more complete evaluation of the pollutant risk inside e.g. microclimate frames and showcases or in exhibition rooms and storage facilities.

By use of passive diffusion gas samplers it was shown that concentrations of pollutants that infiltrate microclimate frames from outside (e.g. the oxidizing pollutants NO_2 and O_3, and SO_2) are usually very low, whereas concentrations of organic pollutants; acetic and formic acid and many other volatile organic compounds (VOCs), that are emitted from materials enclosed by the frames, are typically very high.

The measurements made in PROPAINT of concentrations of the single pollutants were used to calibrate the dosimeters, and the impact measured on the dosimeters was compared with expected impact from the pollutants on cultural heritage objects made from organic materials. A "tolerance–location diagram" was developed for the interpretation of the results from the dosimeter measurements. In the diagram the result for the measured environment is located (plotted) in relation to the expected good (tolerable) environment of cultural heritage locations with a different degree for protection against the outdoor environment.

PROPAINT has shown the applicability of dosimetry to study methods to reduce pollutant concentrations inside microclimate frames and have investigated the use of dosimetry with continuous logging of measurement values.

3.2 Implications of PROPAINT results for preventive conservation

The implications for preventive conservation from the work in PROPAINT, with measurement of pollutants in microclimate frames, can be divided in three categories:

- Measurement methodology
- Impact assessment
- Mitigation methods

3.2.1 Measurement methodology

PROPAINT has developed further from the pre-PROPAINT state of the art the instrumentation for dosimeter measurement and new methodology for interpretation of results obtained from the use of dosimeters. These results are relevant for the evaluation of the quality of indoor environments for cultural heritage.

Piezoelectric quartz crystal dosimeters (RM-PQC and L-PQC) that can measure continuously the generic impact of climate and pollutants have been further developed and tested. The continuous reading makes possible evaluation of rates of change of environments and detection of sudden changes in environmental conditions that can be important for degradation effects on objects and thus for preventive conservation strategy. The holders and

data-loggers for these dosimeters were miniaturized to make possible continuous measurement in small enclosures, such as microclimate frames. A miniaturised holder was also produced for the EWO dosimeter, making all the three types of PROPAINT dosimeters suited for measurement in small enclosures. These developments have made dosimetry a more accessible and useful technology for the evaluation of environments within enclosures and microclimate frames.

3.2.2 Impact assessment

PROPAINT clearly showed that the main pollution degradation risk for paintings inside microclimate frames is the high concentrations and deposition of organic gases inside the microclimate frames, and in particular of the low molecular weight compounds acetic and formic acids. The reason for the high concentration of these gases is their high emission rates from materials inside the microclimate frames, in particular wood, and the very low air exchange rate. It is well known that acetic and formic acid corrode lead, copper, some other metals and calcareous minerals (e.g. Tétreault 2003). Little is however known about the possible long time degradation impact of these gases on diverse organic materials/objects; although it is known that the degree of polymerization of cellulose is lowered by exposure to acetic acid (Strilic 2009, Tétreault 2003, Dupont and Tétreault, 2000).

The research in PROPAINT showed that the existing types of dosimeters were typically sensitive to either photo-oxidizing or acidic impact of the environment. PROPAINT showed that a more complete evaluation of the quality of the environment could be obtained from the combined use and subsequent evaluation of measurement results from two types of dosimeters. Based on this principle and on the evaluation of tolerable environmental conditions in different indoor locations performed in the previous EU MASTER project, novel diagrams for dosimeter results presentation and evaluation were produced. These diagrams make possible an easy and more complete evaluation of the environments for the protection of cultural heritage objects.

Impact assessment with this method can give easy overall evaluation and comparison of indoor environmental quality for cultural heritage locations. In addition, based on the appropriate understanding of degradation mechanisms and on correlation analysis with degradation rates for particular materials, it can be applied for the evaluation of the degradation risk for specific materials. For example, a direct comparison and correlation can be made of the impact on the RM-PQC and the degradation of varnishes of the impact on the L-PQC and the corrosion of lead of the impact on the Glass slide and the corrosion of glass and of the impact on the EWO and the degradation of synthetic polymers. Although dosimeter materials are chosen which are more reactive than actual materials (e.g. reactivity of thin nano-scale thickness lead films on PQC crystals, is much higher than of lead objects, and glass dosimeters have a specially sensitised composition making them more sensitive than other forms of glass). Correlation studies were performed in previous EU projects and during PROPAINT for the different dosimeters, for direct evaluation of degradation risk for such materials. Indirect comparisons can be made for less similar materials, based on comparison of the influence of environmental factors, leading finally to the general evaluation of environments for indoor cultural heritage based on suggested tolerable levels for the environmental parameters.

3.2.3 Mitigation methods

PROPAINT performed some preliminary studies of mitigation methods to reduce the pollutant impact on paintings/objects inside microclimate frames. There is a strong need to do more research in the field of mitigation methods, also related to the sensitivity of materials and objects to pollutants (impact studies).

Measurements and modelling were applied to study the effect of different mitigation methods. The performed investigations focused on two major approaches to the problem related to the design of microclimate frames:

- Effect of air exchange rate and microclimate frame geometry
- Effect of barrier films and absorbers mounted inside microclimate frames.

Effect of air exchange rate and microclimate frame geometry
Mass balance modelling of the pollutant "impact flux" on paintings inside microclimate frames was performed as part of the PROPAINT project. The modelling indicated that ventilation of a microclimate frame is not a very effective way to reduce the organic acid (acetic and formic acid) flux to the paintings. An increase in ventilation from a low air exchange ($< 1\ d^{-1}$) to several air exchanges per hour would not, according to the model, significantly reduce concentrations and impact fluxes of organic acids to paintings (Chapter 6). The reason for this is the low air volumes in frames, and thus small amount of pollutant removed by every single air exchange, as compared to the internal emission and deposition fluxes. Increased ventilation of a microclimate frame also has the disadvantages that it makes the climate buffering less effective and that it increases the influx of pollutants from outside of the microclimate frame.

Effect of barrier films and absorbers mounted inside microclimate frames.
The use of barrier films and absorbers mounted inside microclimate frames are methods that can mitigate the problem caused by an accumulation of internally emitted pollutants inside a microclimate frame. This was not a major topic in the PROPAINT project, but a case study was performed and gave valuable information on the effect of such measures. It was found that the installation of a barrier film, such as PET-covered aluminium, Fomex or Melinex, by themselves or in combination with charcoal cloth, were effective in reducing the impact on pollution sensitive dosimeters inside a microclimate frame. The best effect in these studies was found when using a combination of PET-covered aluminium and charcoal cloth.

3.3 Why measure environments for paintings?

Objects of art such as paintings are subject to degradation due to the ambient environment, such as physical, chemical and biological factors. For valuable objects it is important that this rate of degradation is as slow as possible. Paintings are exposed to an ambient environment that can be very different depending on where they are located. Many factors affect the degradation of paintings over time and thus their observed condition. Physical damage from impacts, shocks during handling or due to other causes is a potentially important and often critical damage factor. The physical and chemical, including biological, interaction between a painting and the surrounding environment over the longer time scale is also very important. For the long term preservation of paintings it is essential that the surrounding environment is as beneficial as possible. Generally, this means a stable environment within the limits of values for e.g. T, RH and pollutants that give the least stress to the objects. A stable environment does not necessarily mean constant environmental conditions, but could mean

that it should not vary outside the limits of e.g. historical fluctuations. Limits for the values of the environment are recommended to avoid critical degradation and retard the degradation as much as practically possible.

When a decision has been made about optimal environmental conditions for cultural heritage objects such as paintings, - based on the available scientific data, observations and experience, it should be the aim to design the location for the object to satisfy or at least approach these conditions. For an art gallery or a museum this could be achieved by the optimal engineering and construction of the building as such, by the construction and design of its exhibitions spaces and storerooms, and/or by the choice and design of microclimates such as microclimate frames, storage boxes and transport cases to be used for additional protection.

Environmental measurements can be used as a research tool to investigate how different building solutions for exhibitions, storage and smaller scale preventive conservation measures influence the conservation conditions for paintings.

Measures that influence conservation can be administrative decisions such as changes in opening times or number of visitors allowed, technical measures such as changes of locations for objects/paintings, changes in regimes for ventilation, light or climate control, or use of additional protection such as microclimate frames, transport cases and storage boxes.

When measures that affect the environment for paintings are taken into account in a building, it is advisable to monitor and record these changes in climate and/or pollutants to know how the conservation conditions and thus long term preservation of the paintings may be affected.

The particular focus of PROPAINT was to investigate the effect of using microclimate frames and varnishes for the protection of paintings against degrading air pollution and climate influences.

3.3.1 Measurement of climate in PROPAINT

In PROPAINT temperature and RH was measured and recorded inside and outside microclimate frames for paintings with and without paintings installed, by standard electronic equipment designed for indoor use in e.g. museums. In addition light was measured as spot readings for a number of locations outside and inside of the microclimate frames and as doses by the application of the LightCheck© ultra dosimeter.

3.3.2 Measurement of pollution in PROPAINT

In PROPAINT both parameter and dosimeter measurements (Chapter 4.3.2.2) were used to develop an improved method for measurement and evaluation of environmental conditions in microclimate frames. Both dosimeters and passive diffusion gas samplers have the advantage that they are small devices that can easily be placed inside a microclimate frame. After placing in position for exposure they usually don’t need further attention before collection.

3.3.2.1 The use of dosimeters in PROPAINT

The three different types of dosimeters used in PROPAINT measured the generic effect of the environment to be compared with the expected degradation impact on paintings. It was found that these dosimeters measured either photo oxidizing or acidic impact and that their combined use made possible a more complete evaluation of the quality of the air environment.

The following dosimeters were used inside and outside of the microclimate frames:

3.3.2.2 Early Warning Dosimeter for Organic Materials

In the EC funded project MASTER (2003-2006; MASTER project, 2009) an *Early Warning dosimeter for Organic materials (EWO)* was developed by the Norwegian Institute for Air Research (NILU), (Figure 4A and Figure 5). The EWO dosimeter is a synthetic polymer sensitive to NO_2 and O_3, and to SO_2 only at high humidity and concentrations, usually emitted outdoors and ventilated or infiltrating to the indoors. It is also sensitive to the climate parameters of temperature and UV light, and it has indirectly been calibrated for RH using RH - T isoperm values (Sebera, 1994). The effects of the environment on the EWO dosimeter was initially measured in 120 periods of 3 months, in 30 locations in 10 European museums, during one year campaign in the EU project MASTER (Grøntoft et al., 2006). Calibration of the dosimeter response against the environmental influences has also been performed. Further, evaluation of tolerable response levels for the EWO, as compared to effects on organic cultural heritage objects, was performed. The evaluation was based on reported degradation impacts of single environmental parameters on heritage objects (Tétreault, 2003) and suggested environmental standards for indoor cultural heritage locations as reported in the literature (ASHRAE, 2007). Tolerable impact levels were suggested for indoor cultural heritage locations with different degree of protection against the outdoors, ranging from archives to outside stores with no control (Figure 6). Tolerable response levels for showcases were set to one level lower than the indoor location.

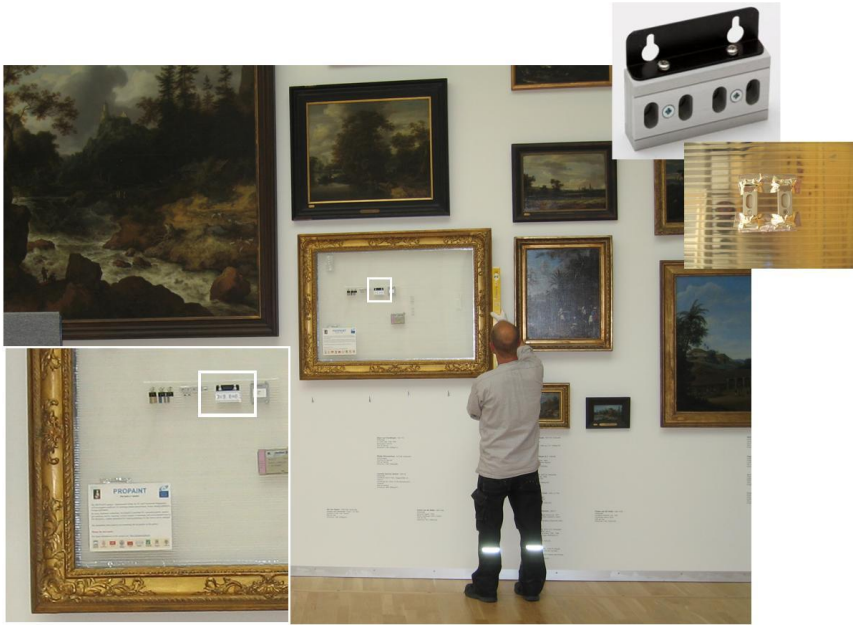


Figure 5: The EWO dosimeter developed at NILU, exposed at Statens Museum for Kunst, Copenhagen, DK. Upper Right; the holder for up to four dosimeters, below the miniaturised holder for one dosimeter.

Determined expectation	EWO-G dosimeter response level after exposure.				
	1	2	3	4	5
Archive store	**Expected environment (acceptable)**	Environment could be better	Environment is poor	Something is wrong with control	Serious problem with building or control
Purpose built museum	Environment is very good	**Expected environment (acceptable)**	Environment could be better	Environment is poor	Something is wrong with control
House museum	Excellent environment	Environment is very good	**Expected environment (acceptable)**	Environment could be better	Environment is poor
Open structure	Dosimeter is not responding	Excellent environment	Environment is very good	**Expected environment (acceptable)**	Environment could be better
External store with no control	Dosimeter is not responding	Dosimeter is not responding	Excellent environment	Environment is very good	**Expected environment (acceptable)**

Figure 6: Table for interpretation of environmental quality for cultural heritage in different locations based on EWO dosimeter results. (Grøntoft et al., 2006).

The EWO dosimeter needs to be exposed for three months on the actual location in the museum/institution. The result reading is performed by UV spectro-photometry after return to the laboratory. The result is reported to the user in a tolerance – location diagram (Figure 6 and Figure 28). In PROPAINT a diagram has been developed and it includes in addition tolerability of the acetic acid concentration or the measured impact of organic acids on a complementary dosimeter (Figure 16).

3.3.2.3 The Piezoelectric Quartz Crystal Dosimeters

Piezoelectric Quartz Crystal (PQC) dosimeters using several types of coatings have been in use at Birkbeck College (UK) in several projects. The PQC crystals when connected in a circuit measure the change in mass of the coating (at the nano level) which is then translated into a frequency shift. Resin mastic coated dosimeters (RM-PQC) were prepared and calibrated for use in the EU funded MIMIC (EVKV-CT-2000-00040) project. Exposure was also performed in museums and historic houses near art works (Odlyha et al., 2005). In the SENSORGAN project (Contract no. 022695), lead coated dosimeters (L-PQC) were deposited, tested in the laboratory under controlled conditions, and then used to test the air passing from the wind chest into the lead-based pipes of historical organs (SENSORGAN, 2009). The rationale for the use of natural varnishes was to mimic the behaviour of natural varnishes used to protect paintings, and for the use of lead to mimic the behaviour of lead-based pipes in historical organs. In both cases the response of the PQC dosimeter was many times more sensitive than that of the objects, and in both cases varnish coated strips and lead coupons were also exposed. This provided additional material for chemical analysis.

The coated array of eight crystals (four of each) was housed in a small chamber exposed to the air (Figure 4 B). Inside the microclimate frames, where size restricted the use of arrays of

eight PQC-dosimeter crystals (four RM-PQC and four L-PQC), two to four crystals clamped between steel plates were suspended within the microclimate frames. The frequency shift for the PQCs was measured before and after the exposures, and was calculated as the % change in frequency or (Hz/kHz) shift in frequency. L-PQC values are only compared between themselves, as are RM-PQC values, and the different units can be compared to results in Odlyha et al. (2005) and SENSORGAN (2009). High values of change correlated with the presence of high levels of photo-oxidising agents (RM-PQC crystals) and high levels of volatile organic acids (L-PQC). A new miniaturised prototype for measuring the frequency shift of the crystals in real time has been developed within the PROPAINT project for use within the restricted environment of the microclimate frames (Figure 7).

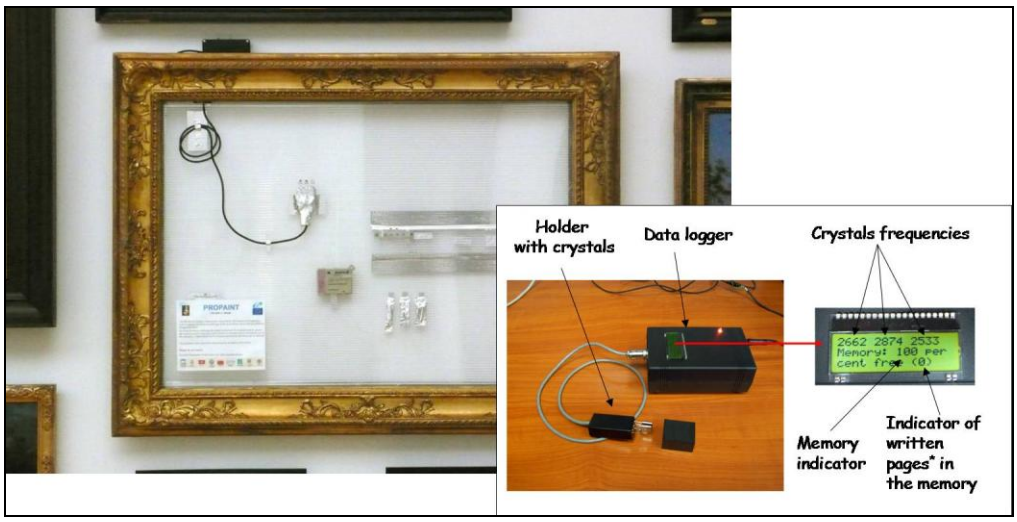


Figure 7: The PQC dosimeters for continuous operation, developed by Birkbeck, exposed at Statens Museum for Kunst, Copenhagen, DK.

3.3.2.4 The Glass Slide Dosimeter

The Glass Slide Dosimeter (GSD) from Fraunhofer ISC consists of a thin glass chip of fire polished potassium- and lime-containing silicate glass, highly sensitive to various atmospheric impacts (Figure 4C and 8), (Mottner, 2006, 2007). Environmental influences like humidity, air pollutants or emitted organic acids cause a deterioration process which alters the surface layer by leaching of potassium and calcium ions, formation of a gel layer and finally by the formation of corrosion crusts. This effect can easily be measured and quantified by FTIR spectroscopy as an increase in the intensity of the OH stretching band, - related to the increasing water content in the affected glass surface - at 3300 cm^{-1}, to assess the potential damage risk on the objects, indoor and outdoor (e. g. artworks, constructions). The dosimeter system employed within the PROPAINT project was first developed during the EC-funded project AMECP: Assessment and Monitoring the Environment of Cultural Property, EV5V-CT92-0144 (1993-1996). In Germany, the method is registered since 1992 as German Technical Guideline VDI 3955/2: Assessment of the corrosive effects of complex environmental conditions at materials: exposure of glass sensors (ed.: VDI, Dusseldorf; Beuth Verlag GmbH, Berlin, Germany). The GSDs have for the last 15 years been applied widely as an environmental impact dosimeter for cultural heritage, indoors in museums, in showcases, and outdoors. In general, to evaluate the utility of the GSD dosimeters for PROPAINT measurements, different kinds of Glass slide dosimeter compositions available at ISC for monitoring different atmospheric impacts (types M1.0 with 3 different surface finish

treatments, MI, M2, and M5), were exposed. The dosimeter type that was found to be best suited for indoor museum room and showcase measurements over the last 15 years (M1.0 with fire polishing finish), and showed the best sensitivity and linear behaviour, was used in PROPAINT.

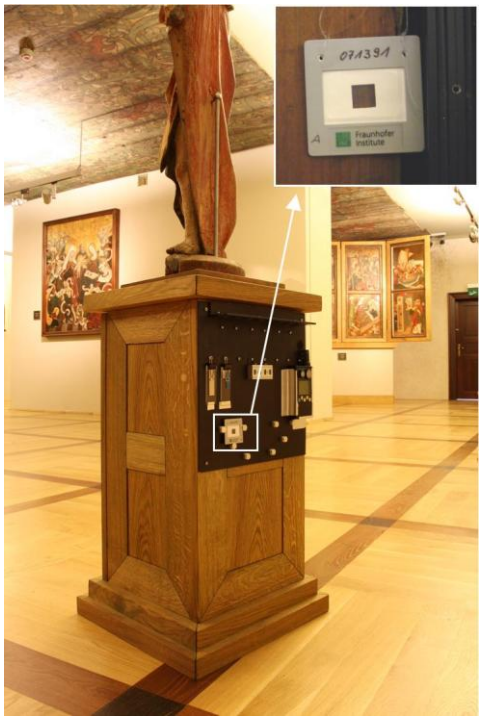


Figure 8: The Glass Slide Dosimeter developed by Fraunhofer ISC, exposed at the National Museum in Krakow, Poland.

In Figure 9, the range of possible and observed Glass Dosimeter results (ΔE-values) are shown together with related evaluation criteria for environmental risk potential regarding artworks.

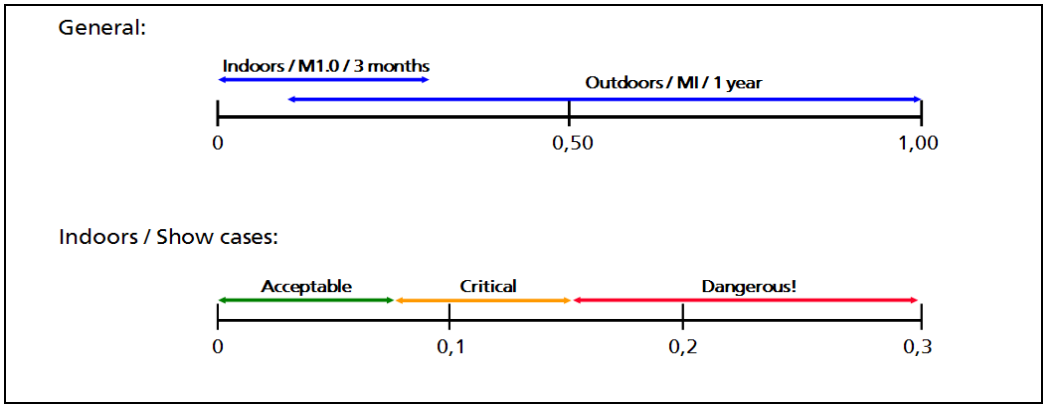


Figure 9: Environmental Glass Slide Dosimeters (type M1.0 and MI): range of exposure results (ΔE-values) and related evaluation criteria after 3 month exposure (see also Figure 14).

The assessment of the risk potential is based on a high number of environmental investigations on cultural heritage objects performed during the last 15 years. Two different dosimeter glass compositions are used for either indoor or outdoor exposure. While for outdoor exposure (duration typically 1 year) ΔE-values with a maximum of 1.0 were measured, the ΔE-results for indoor monitoring (duration typically 3 months) usually lie in a range between 0.0 and 0.3. Values < 0.07 were quantified as moderate and acceptable for an indoor museum atmosphere, showcase or microclimate frame for paintings. Values in the range $0.07 < \Delta E < 0.15$ were termed as critical micro climate conditions, while results with $\Delta E > 0.15$ were found to represent dangerous atmospherical conditions for artworks in storage, transit or during exhibition. This estimation is, nevertheless, based on empirical data and the observed preservation state of cultural objects. The GSD dosimeter system has been available on the market since 1997. It is shipped and applied worldwide and can be ordered directly at Fraunhofer ISC, Germany.

To provide a better basis for the evaluation of Glass Dosimeter results within the PROPAINT project, experiments where the Glass Dosimeters were exposed to various well defined atmospherical concentrations of acetic acid were set up and the corrosion/leaching behaviour of the dosimeters was observed. As for the field studies, exposure time was chosen (calculated) to 3 months. The Glass Dosimeter systems turned out to be especially sensitive to the environmental impact of acetic acid, more than to formic acid/formaldehyde and much more than to oxidative attack.

For the experiments artificial equilibrium acetic acid concentrations ranging from 270 $\mu g/m^3$ to 5.34 mg/m^3, were produced in special reaction vessels, to represent the possible 'real' pollution values observed in field studies. The results of the exposures are shown in Figure 10. Available PROPAINT results from passive sampling of acetic acid and the measured ΔE-values for the GSDs inside the microclimate frames of the PROPAINT end-user museums, are displayed for comparison (Figure 10). In addition the range for the results values from a previous dosimeter study performed by ISC in the Green Vault Dresden (Germany), where acetic acid values from a single gas measurement campaign are available, are shown in the diagram.

Figure 10 shows strong (almost linear) dependence of the GSD result-values (ΔE) on the acetic acid equilibrium concentrations measured in the field exposures. The GSD results from the laboratory exposures were about twice as high as those measured within the end-user microclimate frames in PROPAINT for the same concentrations. This observation probably shows the strong effect of relative humidity on the Glass Dosimeter reactivity. The relative humidity was higher in the laboratory reaction vessels than in microclimate frames in the museums.

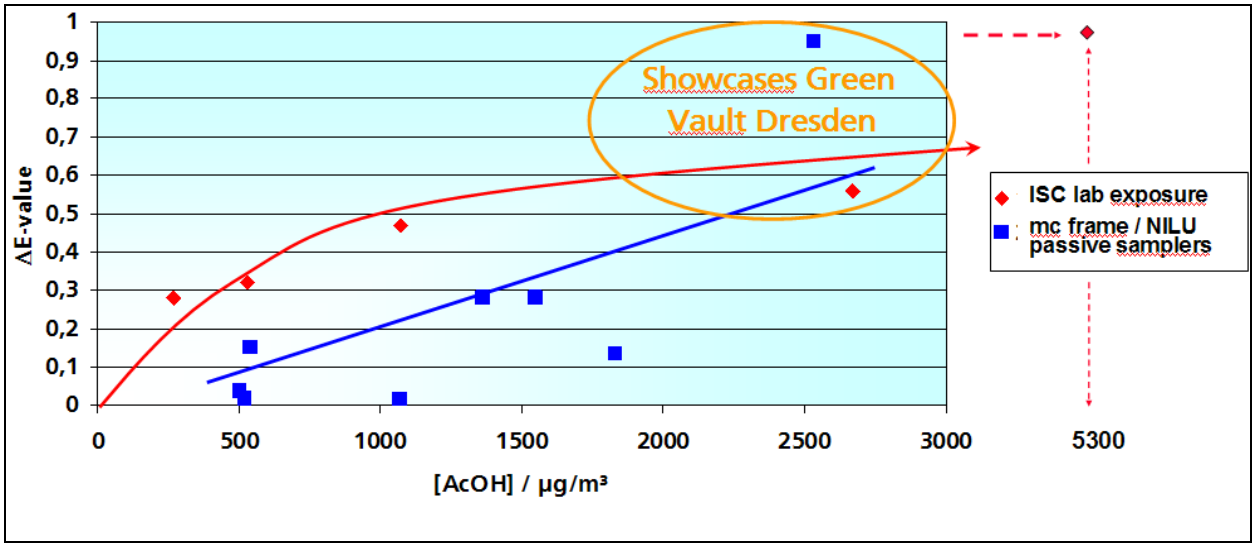


Figure 10: Environmental Glass Slide Dosimeters: correlation of ΔE-values (3 months exposure) after acetic acid exposure vs. acetic acid concentration (all available data).

The technical specifications, measurement methodology, previously found environmental sensitivity and determined impact levels for cultural heritage objects for the three dosimeters are reported in the following references: Grøntoft et al. 2006, MASTER project 2009, Mottner 2006, 2007, Odlyha et al. 2005 and SENSORGAN 2009.

A problematic environment, as detected by dosimeter measurements, can be regarded as a "first warning". If the results from the dosimeter measurements are not sufficient for precise diagnosis of the problem, more specific measurements of climate and pollution conditions can be performed.

In addition to the three different dosimeters that were applied in PROPAINT lead coupons, of size 20 mm x 10 mm and weight 500 mg +/- 0.01 mg, were exposed with the L-PQC dosimeters. The weight change of the lead coupons was measured. Basically, the impact levels on the dosimeters were determined by comparing the observed and reported impact by a combination of single environmental parameters on cultural heritage objects (Tétreault 2003) with the known impact of the same parameters on the dosimeters.

In the previous EU projects, and continuing in PROPAINT, the GSD, EWO and the PQC dosimeters were calibrated against the effects of generic building environments, supported by literature information (e.g. Sebera, 1994; Tétreault, 2003), on the deterioration of materials. In PROPAINT the impacts on the dosimeters were compared. This clearly showed the complementary nature of these dosimeters. The dosimeters were found to be sensitive to either photo-oxidizing or acidic impact. A procedure for simultaneous measurements with two complementary dosimeters, with presentation of results in a so called "location-tolerance" diagram for evaluation of the quality of the environment for cultural heritage objects, was produced. This new combined use of dosimetry gives a more complete evaluation of indoor environmental impact on heritage objects.

The calibration procedure was performed to scale the impacts observed on the dosimeters with those expected on organic objects such as paintings. However, for a more accurate evaluation of risk to single materials the general evaluation criteria determined for the

dosimeters in PROPAINT should be complemented with particular information about reaction mechanisms and rates of degradation for the particular materials of interest.

3.4 Sampling locations

All the dosimeters (i.e. PQC, EWO and GSD) were exposed simultaneously for three months (2007/08) inside and immediately outside microclimate frames for paintings in different end-user locations around Europe and overseas (Table 3). The exposure locations comprised one workshop with an international transporting and frame design company SIT-Artyd laboratories (Madrid, Spain), 12 locations in 11 end-user museums in Europe and Mexico and one microclimate frame in transit. The locations within museums deliberately included different types of building and exposure, ranging from fully air-conditioned and filtered stores to exposed and unconditioned display in busy city centres. In addition to the monitoring inside and outside of the microclimate frames, environmental sampling was performed in a showcase at the Uffizi Gallery in Florence, Italy and in a storeroom at the Centre for Conservation Science and Restoration Techniques, National Research Institute of Cultural Properties, Tokyo, Japan.

*Table 3: The locations for exposures in microclimate frames in PROPAINT*** .*

Locations	Mc-frame characteristics			
	Type of mc-frame*	Ventilation rate (day^{-1}) **Net V(m^3)**	Age. Major materials**	Location ** AC = Air conditioned N = Naturally ventilated
1. SIT-Artyd workshop, Madrid, Spain	M	0.19 **0.077**	New 2007. Synthetic polymers, methacrylate, polycarbonate. Stainless steel. Acrylic paint, Chloroform bonding. Aluminium.	Workshop (AC) Pollutants from materials, and adjacent rooms.
2. NG. National Gallery, Oslo, Norway	H	0.67 **0.013**	30-40 years. Wood. Polycarbonate. Al tape.	Public gallery (N) Painted wallboard. Cork.
3. EH.A.H. English Heritage, Apsley House, London, UK	H	0.17 (-)	Refitted 2007. Al-foil covered wood.	Public gallery (AC) Chemically filtered. Stone building. Silk. Plaster. Carpet. Brick. Wood.
4. EH.K. English Heritage, Kenwood, London, UK	H	1.4 **0.041**	1980s. Al-foil covered wood.	Public gallery (N) Plaster. Wood.
5. Tate B. Tate Britain, London, UK	H	8.6 **0.010**	100 years. Soft wood. Oil tempered hardwood. Gesso. Gilding.	Unconditioned stairwell (N) Well ventilated. Central London. Paint. Plaster. Brick. Wood. Old building.
6. Tate S. Tate Store, London, UK	H	6.7 **0.027**	1990s. Softwood. Oil tempered hardwood Gesso. Gilding. Melinex (polyester) sheet. Gummed brown kraft paper	Conditioned store room (AC) Central London. Cement. Paint, Vinyl. Wood. Other frames.
7. SMK1. "Statens Museum for Kunst" 1, Copenhagen, Denmark	H	0.39 **0.024**	18^{th} or 19^{th} Cent. Mc-frame in 2007. Acryl. painted balsa. Polycarb. Felt. Cork. Al-tape.	Public gallery (AC) Painted gypsum walls. Lacquered wood.
8. SMK2. "Statens Museum for Kunst" 2, Copenhagen, Denmark	H	(-) **(-)**	(-)	In transit with painting, later empty in museum workshop
9. MBV. Fine Art Museum, Valencia, Spain	M	0.15 **0.029**	2005. Synthetic polymers, methacrylate, polycarbonate, neoprene. Volera-, silicon-, Al-tape. Artsorb.	Public gallery (AC) Bricks. Plaster. Stone. Steel. Painted MDF.
10. MNA. National Museum of Art, Mexico City, Mexico	M	(-) **(-)**	New (2007) SIT-Artyd microclimate frame. Synthetic polymers.	Public gallery (AC) Wood. Plaster.
11. GNM. Germanic National Museum, Nurnberg, Germany	H	(-) **0.047**	6 years old. Lacquer covered Al. Rubber sealing.	Public gallery (N) Stone.
12. NMK1. National Museum in Krakow (Leonardo frame), Poland	O	15 **0.32**	5 years old. Fibreboard covered with tapestry	Public gallery (N) Waxed wood. Tapestry. Lime plaster and emulsion paint. Glass ~ 60 % of this enclosure.
13. NMK2. National Museum in Krakow (new microclimate frame), Poland	H	0.42 **0.060**	2007. Polycarbonate. Al profiles and foil.	Public gallery (N) Lacquered wood. Acrylic painted lime plaster. Gypsum boards.

* M = "Modern" new built. H = "Historic" modified. O = Open microclimate enclosure. **Glass in microclimate frames and rooms is not included. (-) = not available. *** Measurements were also performed in a showcase in the Uffizi, Italy and in a storeroom Japan (Figure 12).

.

Two general types of microclimate frame designs were tested: “Modern” new microclimate frames purpose built by the SIT-Artyd Company and “historical” microclimate frames adapted to existing picture frames (Figure 11 and Table 3). In location no. 12 (Table 3) the painting was placed in a more open purpose built glass enclosure with glass (front and sides) fitted to the wall (Figure 11C). Measurements were also performed in a showcase located in the Uffizi Gallery, Florence, Italy (Figure 11D).

Figure 11: Three dosimeters: 1. Early Warning Organic (EWO) dosimeter 2. Resin Mastic (RM-PQC) and Lead Piezoelectric Quartz Crystal (L-PQC) and 3. The Glass Slide Dosimeter (GSD), mounted inside the “modern” SIT-Artyd microclimate frame (A) and a “historic” frame adapted to microclimate frame at English Heritage, Apsley House, London, UK (B). C: Glass enclosure for painting (National Museum in Krakow). D: Showcase (Uffizi Gallery).

All sites except four (No 1, 5, 6 and 7, Table 3) had paintings installed in the microclimate frames. The SIT-Artyd microclimate frame (No 1, Table 3) was arranged as a “worst case scenario” and a fresh oak panel prepared with a natural varnish and a polyvinyl acetate (PVA) containing old white carpenter‘s glue was installed.

Additional standard passive sampling of pollutant gases was performed simultaneously inside and outside the microclimate frames in two periods following the dosimeter exposures. VOCs were sampled with Tenax tubes over one week. Then NO_2, O_3, SO_2, acetic and formic acid were sampled over one month with separate passive diffusion gas samplers (Ferm, 1991). In addition formaldehyde was sampled with SKC UMEx100 passive samplers. For the NO_2 and acetic acid results that are reported or used in this work the detection limits have been found to be 0.03 and 0.5 µg m^{-3}, respectively. For the SO_2 it is has been found to be 0.1 µg m^{-3}. For the O_3, the detection limit is reported to be 1 µg m^{-3}. For the formaldehyde sampler the detection limit is reported to be 0.05 µg m^{-3}. The air exchange rates (ventilation rates) of the microclimate frames were determined in individual single experiments from the decay of the

concentration of CO_2 initially injected as a tracer gas (Calver et al. 2005). The temperature and relative humidity (T and RH), was recorded during the dosimeter exposures by the standard electronic equipment available to the conservator at each location.

3.5 Main results from the measurement campaigns

Figure 12 shows exposure locations in the end-user institutions. The measurements in PROPAINT were divided between a general measurement campaign and different case studies. In addition to the dosimeters, passive diffusion gas samplers and climate measurements, the air exchange rates of the microclimate frames were measured in the general campaign. The general measurement campaign included all locations (Table 3). The case studies focused on specific concerns and were carried out at selected locations (see Chapter 4.6). (Results for four additional frames located in the SIT workshop are given in Appendix 1).

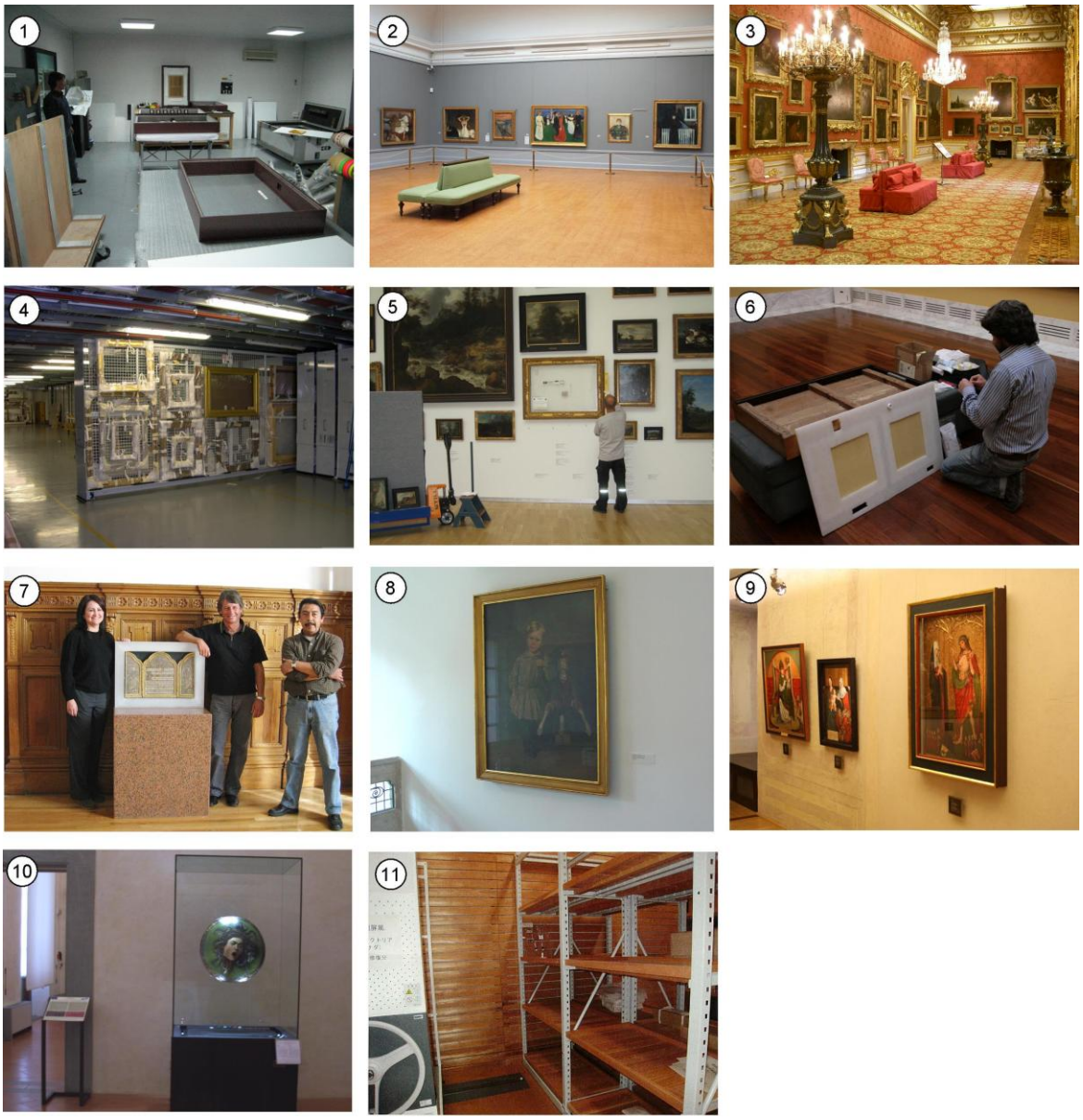


Figure 12: End-user locations of the PROPAINT project (Table below).

No	Institution	Acronym
1	SIT – laboratories, Madrid, Spain	SIT-Artyd
2	Nasjonalmuseet for Kunst, Arkitektur og Design, Oslo, Norway	NG
3	English Heritage, Apsley House, London, UK	EH
4	Tate Store, London, UK	Tate S (store) and Tate B (Britain)
5	Statens Museum for Kunst, Copenhagen, Denmark	SMK
6	Fine Arts Museum, Valencia, Spain	MBV
7	National Museum of Art, Mexico City, Mexico	MNA
8	Germanishes Nationalmuseum, Nürnberg, Germany	GNM
9	National Museum in Krakow, Poland	NMK
10	Uffizi Gallery, Florence, Italy	Uffizi
11	Centre for Conservation Science and Restoration Techniques, National Research Institute of Cultural Properties, Tokyo, Japan	CCSRT - NRICP

3.5.1 Dosimeter measurements

In Figure 11 it is shown how the three major types of dosimeters were exposed inside the two different types of microclimate frames and Figure 13 shows the placement of dosimeters outside the microclimate frame at one location.

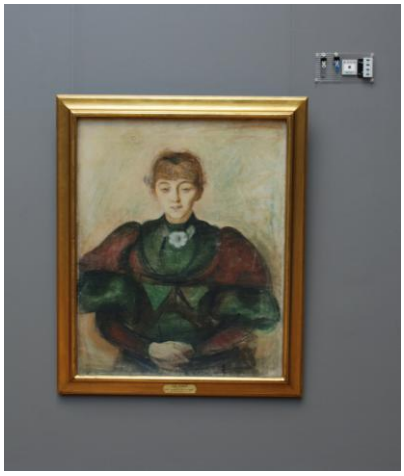


Figure 13: The Dosimeters placed outside the microclimate frame with a painting made by Edvard Munch, Nasjonalmuseet for Kunst, Arkitektur og Design, Oslo, Norway.

The EWO and RM-PQC dosimeter measurements showed higher response outside than inside microclimate frames for paintings. Whereas L-PQC and GSD responses were higher inside than outside the microclimate frames (Figure 14). The EWO and RM-PQC measurements show that the control of pollutant infiltration, or possibly of climatic and UV conditions, in some of the end-user museums is less than good. The lower values for the RM-PQC and EWO in the microclimate frames than in the rooms indicate the protective effect of the microclimate frames against the oxidizing gases, and that the microclimate frames may have shaded the dosimeters against light exposure.

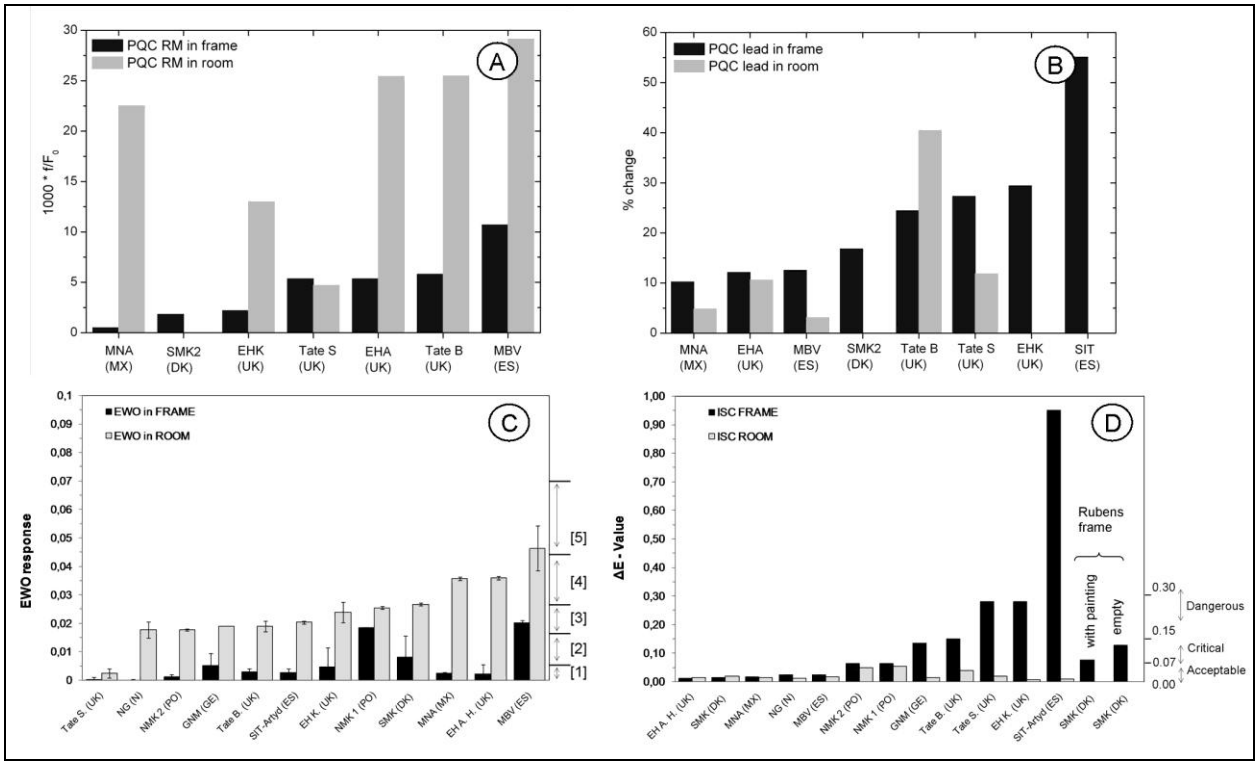


Figure 14 Dosimeter results obtained inside and outside microclimate frames for paintings with (A): The Resin Mastic PQC dosimeter (f / F_o = relation between the frequency shift and the original coated crystal frequency, KHz). For SMK2 measurement was not performed outside the microclimate frame. The standard deviation for the measurements ranged from 0.66 to 1.0 with unit $1000*f/F_o$. (B): the Lead PQC dosimeter (Change (%) in frequency or mass). In the case of SMK2, EH.K and SIT-Artyd, measurements with L-PQCs were not performed in the rooms. For the other rooms no response was detected. The standard deviation for the measurements of the L-PQCs ranged from 0.12 to 0.22 %. (C): The EWO dosimeter (average of two parallel exposures, except in GNM room. The EWO response is in absorption units at 340 nm). SMK = SMK1. Number in brackets are tolerability location levels [11] (at RH = 55%): [1]: Archive store, [2]: Purpose built Museum Gallery, [3]: Historic House Museum, [4]: Open display in open museum, [5]: Outside store with no control. (D): The Glass Slide Dosimeter. (ΔE - Extinction values measured as IR absorption at 3300 cm^{-1}). (SMK = SMK1, "Rubens frame" = SMK2).

A set of measurements were performed in a microclimate frame in transit between Copenhagen and Holland. The microclimate frame was made by Statens Museum for Kunst, for a painting made by Rubens (SMK2, Table 3). After the Rubens painting returned to Copenhagen, measurements were performed inside and outside of the empty microclimate frame exhibited at Statens Museum for Kunst in Copenhagen. (See Chapter 4.6.2, and also Figure 7 which shows PQC dosimeter exposed in this frame).
Figure 15 shows the results from the exposures of the four kinds of dosimeters. Only the EWO and GSD dosimeters were exposed in all three locations. (L-PQC and RM-PQC values for the empty frame are missing in the diagram)

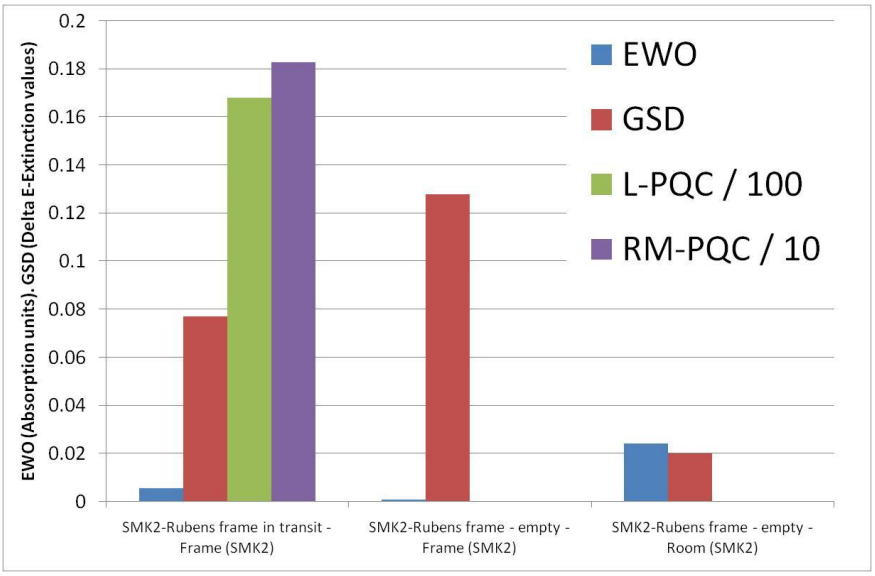


*Figure 15: Results from exposures of the EWO, GSD. L-PQCs and RM-PQCs inside and outside the SMK2 microclimate frame (Table 23). The units for the L-PQC and RM-PQC are % change and 1000*f/F (= relation between the frequency shift and the original coated crystal frequency), respectively.*

The results from the "Rubens frame" (SMK2; Figure 15) did, as for the other microclimate frames (Figure 14), clearly show the different situation with low potential impact of infiltrating oxidants (EWO – "Archival situation"), but high potential impact of organic acids emitted inside the microclimate frame (GSD – "critical situation"). Somewhat higher photo-oxidant impact was measured inside the microclimate frame in transit and lower impact of the organic acids than for the empty frame after the painting was removed. This indicated that the frame in transit was somewhat less well sealed than the empty frame. The lower impact of organic acids in the frame with the painting in transit could however also be due to net deposition on and thus removal of inside pollutants to the painting. The results for the L-PQC and RM-PQC also show the higher impact on the L-PQC, although it seems to indicate a somewhat less "critical" situation than the GSD (Figure 15 and Figure 16). A low value was measured for the RM-PQC confirming the conclusion from the EWO measurement. The situation in the room was quite typical and in the same category as for other PROPAINT end-user museum locations (Figure 14 and Figure 15).

Measurement results for the GSD, L-PQCs and the lead coupons clearly show different conditions with respect to VOCs, and mainly acetic acid, inside and outside the microclimate frames. The results (Figure 14) similarly indicate that the microclimate in the SIT-Artyd "worst case" model microclimate frame is characterized by a very high "dangerous" pollution concentration. The high values observed inside the microclimate frames at English Heritage Kenwood, Tate S, Tate B, and Germanic National Museum were probably due to organic emissions such as formaldehyde and acetic acid, as was found in the dosimeter surface crystals (present as formate and acetate salts) exposed at the SIT-Artyd location.

The results for the L-PQC and RM-PQC and the GSD and EWO dosimeters, respectively, are presented together in the evaluation charts (Figure 16A and B). The charts order the dosimeter measurement results in tolerability location levels from one to five. The levels were based on literature values for the observed degrading effect of single parameters and calculated from

the dose-response functions reported below (Table 5). For the Glass Slide Dosimeter levels 1 – 3 are equivalent to the category "acceptable", level 4 to the category "critical" and level 5 to the category "dangerous" (Figure 9).

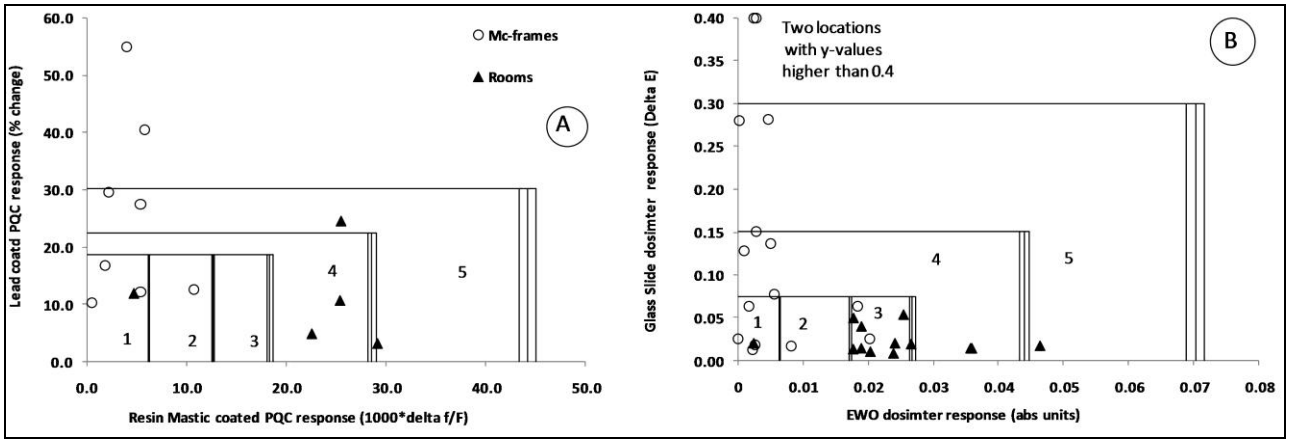


Figure 16: Location-tolerance diagrams with threshold values (Figure 6) for cultural heritage objects in indoors locations. A: Results from RM-PQC (x-axis) and L-PQC (y-axis) (Figure 5 and 9) and B: from EWO (x-axis) and GSD (y-axis) (Figure 6 and 7). The number given in the diagrams are tolerability location levels (at RH = 55%): [1]: Archive store, [2]: Purpose built Museum Gallery, [3]: Historic House Museum, [4]: Open display in open museum, [5]: Outside store with no control, as determined in the EU project MASTER. The close vertical lines are the RH dependence for each level (RH = 45%, 55% and 65%).

The complementary properties of the L-PQC and RM-PQC (Figure 16A), and the Glass Slide and EWO dosimeters (Figure 10B) are clearly seen. Whereas the L-PQC and the Glass Slide Dosimeters measured the acidic properties of the atmosphere the RM-PQC and EWO dosimeters measured the photo-oxidizing properties of the atmosphere. As can be seen from Figure 16 the inside of the microclimate frames are more often exposed to high levels of the organic acidic components where as the photo-oxidizing effect is usually higher in the museum rooms. The complementary properties of the dosimeters give added value to their combined use.

The values for the dosimeter measurements are reported in Appendix 1, Table 1.

Good correlation was observed between the measurements obtained with the RM-PQC and EWO dosimeters (Figure 17A) and the measurements obtained with the L-PQC and the Glass Slide Dosimeters (Figure 17B). The correlation shows that the two systems (i.e. L- and RM-PQCs, and GSD and EWO dosimeters, Figure 17) measure the same properties of the environments and that they are very much interchangeable methods for this kind of indoor environmental evaluation. The PQC dosimeters have the additional property that it can give a continuous on-line measurement for the accumulated impact and rate.

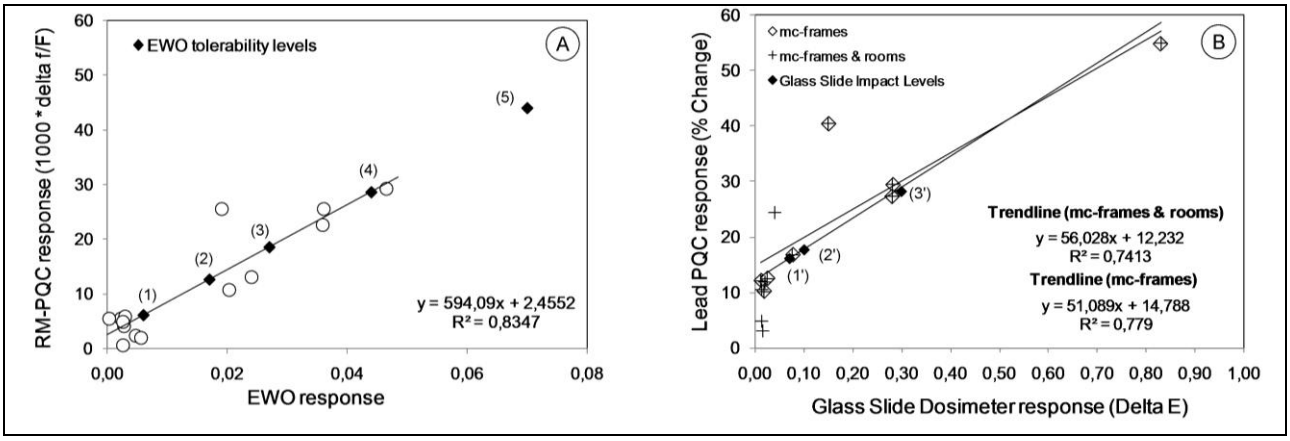


Figure 17: Correlation between dosimeter responses in microclimate frames and rooms. A: EWO and RM-PQC with locations tolerability levels (Figure 14C and A). B: GSD and L-PQC with impact levels (Figure 14D and Figure 15B).

3.5.2 Passive diffusion gas sampler measurements

In the PROPAINT project, passive diffusion gas samplers were exposed inside and outside microclimate frames in the sampling locations where the dosimeters were also exposed. The sampling period was one month and the samplers were returned to NILU for their analyses after the exposures.

Sulphur dioxide (SO_2), nitrogen dioxide (NO_2), ozone (O_3), organic acids (acetic and formic acids), formaldehyde and VOCs (Volatile Organic Compounds) were measured. Inorganic gases, such as NO_2, SO_2 and O_3, are formed mainly outdoors and infiltrates to the indoor environment, and into microclimate frames. NO_2 and O_3 were measured inside nearly all the microclimate frames, varying between 1 and 5 µg m^{-3}, and 1 and 7 µg m^{-3}, respectively (Figure 18). SO_2 concentrations inside microclimate frames were generally very low (< 0.5 µg m^3).

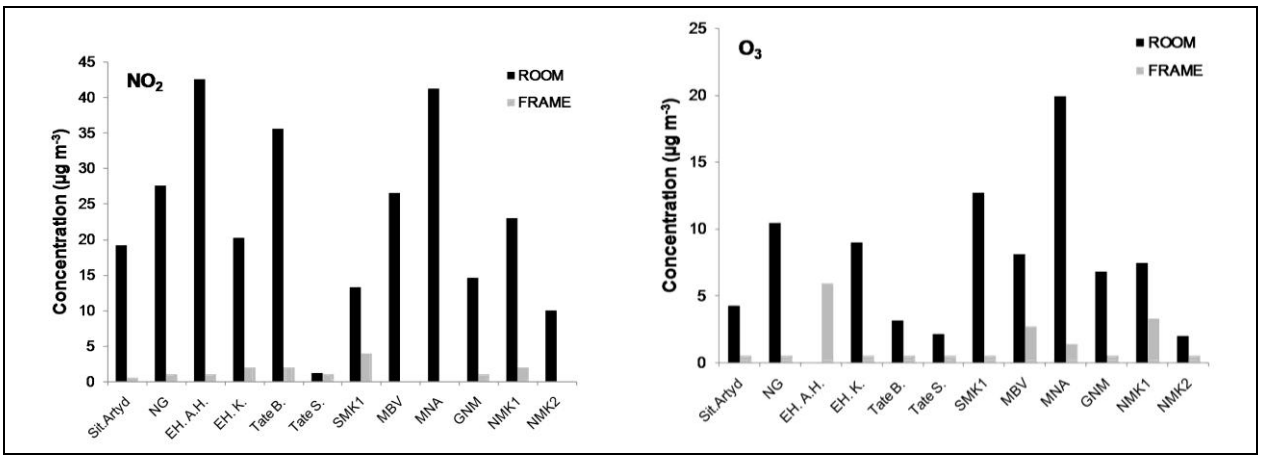


Figure 18: Concentrations of NO_2 and O_3 measured inside and outside microclimate frames. For location abbreviations see Table 3 and table in Figure text 12.

The measured concentrations of organic compounds inside microclimate frames were generally much higher than those for the inorganic compounds (NO_2, SO_2, O_3). Organic

compounds are emitted by materials commonly used in the construction of microclimate frames and from the objects inside the frames. Measurements inside the microclimate frames showed acetic acid concentrations varying from 30 to 2000 µg m^{-3}, formic acid between 30 and 500 µg m^{-3}, formaldehydes between 1 and 6 µg m^{-3} and TVOC between 100 and 5000 µg m^{-3} (Figure 19).

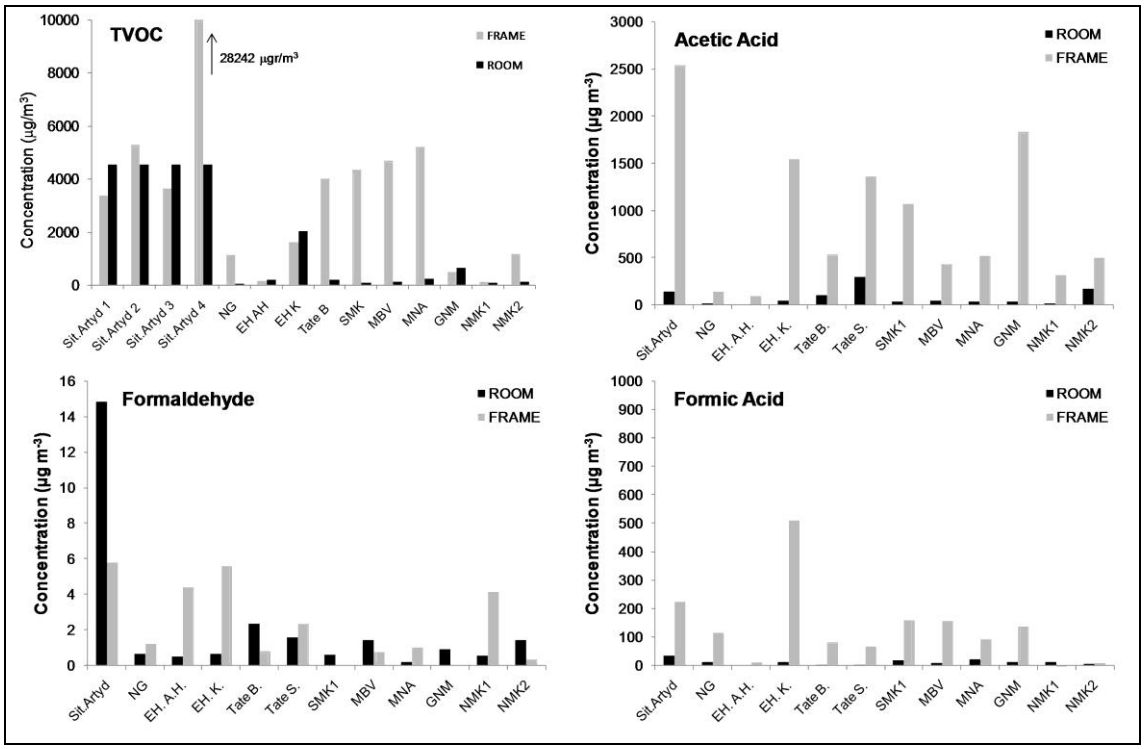


Figure 19: Total concentration of volatile organic compounds (TVOC), acetic acid, formic acid and formaldehyde measured inside and outside microclimate frames. For location abbreviations see Table 3 and table in Figure text 12.

A wide variety of organic compounds was measured inside the microclimate frames. The most frequently measured compounds were α-pinene and limonene which were observed in 13 out of 14 microclimate frames (Figure 20). The highest concentrations of α-pinene and limonene were measured in the empty microclimate frame in Tate Britain (2 263 µg m^{-3}) and in the empty microclimate frame no. 2 of SIT-Artyd (206 µg m^{-3}), respectively. Toluene was also widely measured in nearly all microclimate frames (12 out of 14 microclimate frames), with concentrations varying from 5 µg m^{-3} to 1 103 µg m^{-3} (frame no. 2, SIT-Artyd). Chloroform, 2-methyl-2-propenoic acid methylester, 2-ethyl-1-hexanol and 3-carene were measured at high concentrations (> 500 µg m^{-3}) in some of the microclimate frames (Figure 20).

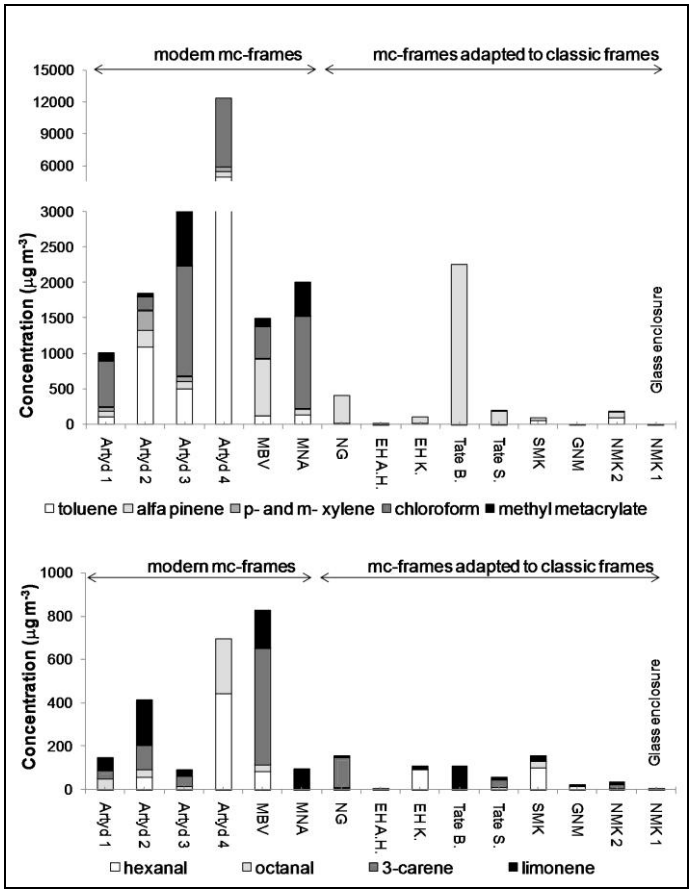


Figure 20: Concentration of specific VOC inside "modern" microclimate frames and microclimate frames adapted to "historic" frames including the glass enclosure. For location abbreviations see Table 3 and table in Figure text 12.

The values for the passive diffusion sampler measurements are reported in Appendix 1 Table 2.

3.5.3 Climate, light and air exchange measurements

Mean temperatures inside the microclimate frames ranged from 15.2 ºC to 21.9 ºC (Figure 21) with an average of 17.8 ºC. In the room locations where the microclimate frames were exposed, the temperature varied from 15.6 ºC to 21.7 ºC (Figure 21) with an average of 18.8 ºC.

The mean relative humidity inside the frames ranged from 38 to 59 % with an average of 52 %, and in the rooms from 25 % to 55 % with an average of 43 %, showing an average buffering effect of the microclimate frames giving reduced humidity variation and increase in average humidity both of 9 % RH (Figure 22).

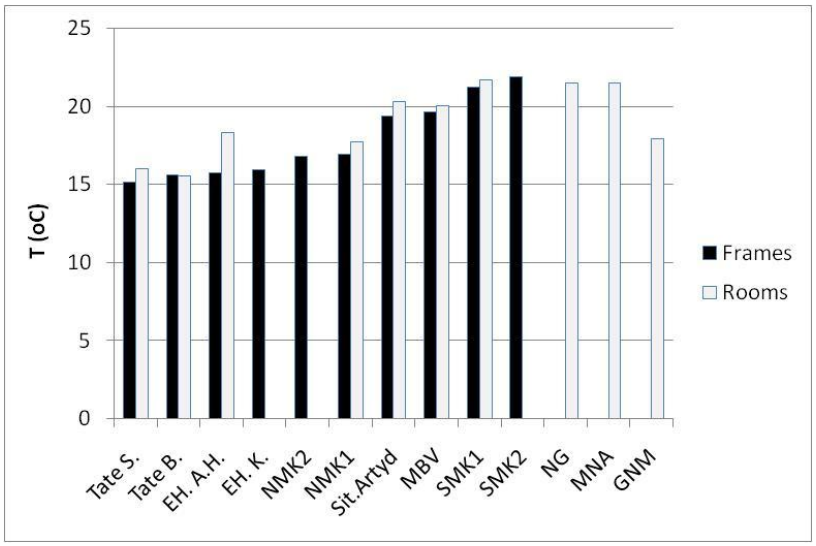


Figure 21: Mean temperature measured inside and outside the microclimate frames for paintings. For location abbreviations see Table 3 and table in Figure text 12.

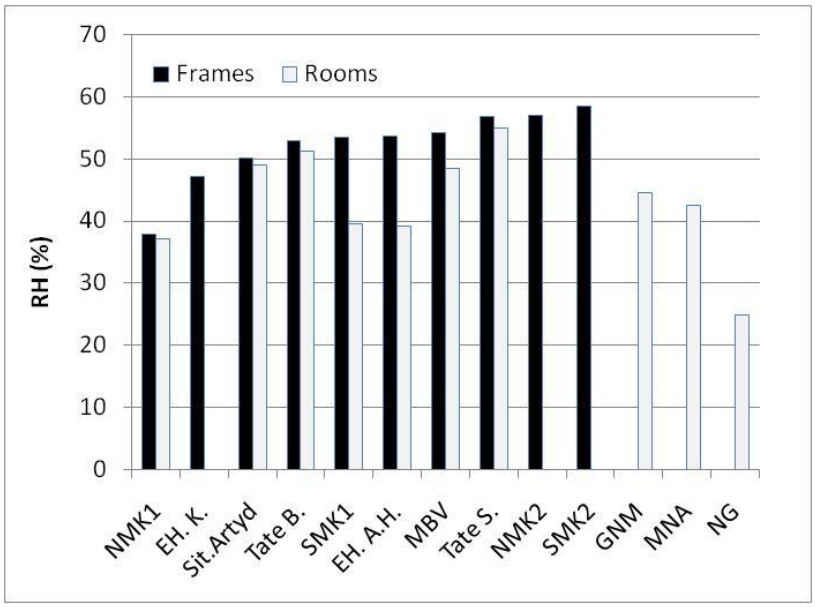


Figure 22: Mean relative humidity measured inside and outside the microclimate frames for paintings. For location abbreviations see Table 3 and table in Figure text 12.

Table 4 shows available results from the light measurement from the use of light dosimeter (LightCheck©), light data loggers and/or measurement performed at one point in time.

The annual luminous exposure was higher in the room than inside the microclimate frames (Table 4) indicating that the microclimate frames protect against light exposure. The accepted annual luminous exposure limits for artefacts such as oil paintings, tempera, wood, polychrome sculptures, bone or ivory is suggested to be 100 000 Lux hours in a year (Tétreault, 2003). The values measured in the microclimate frames for paintings in PROPAINT were above this limit both outside and inside the microclimate frames, for all but one location (Table 4).

Table 4: Light measurements at the sampling locations, obtained by light dosimeter (LightCheck©) and/or sensors. The dose values were normalized to 1 year dose exposure.

	LightCheck© Measurement Dose (1 year; Lux hours)		Measurement by Logger/Sensor Dose (1 year; Lux hours)		
Location	**mc-frame**	**Room**	**Frame**	**Room**	**UV (mW / m2)**
National Gallery, Oslo	725 852	1 388 587	3 153 600	3 652 920	0.0 (F); 0.4 (R)
English Heritage, Apsley House				204 984	
English Heritage, Kenwood				103 280	
Tate Britain				251 937	
Tate Store					
Staten Museum for Kunst	1 303 571	2 105 769		2 952 120	
Fine Art Museum, Valencia					
National Museum of Art, Mexico					
Germanic National Museum		1 330 729			
National Museum in Krakow 1					F = 23 (std 9.4)
National Museum in Krakow 2			43 800		
Galleria degli Uffizi	1 955 357	1 955 357			

Large variation in air exchange rates were measured for the microclimate frames and enclosures investigated in PROPAINT, varying from almost airtight to highly ventilated. Air exchange rates between 0.15 and 1.4 day^{-1} were measured in seven out of 10 microclimate frames (Figure 23). Air exchange rates of 6.7 and 8.6 day^{-1}, were measured in the microclimate frames located in Tate Store and Tate Britain, respectively. The highest air exchange rate was measured in the glass enclosure located in the National Museum in Krakow, approximately 15 day^{-1} (Figure 23).

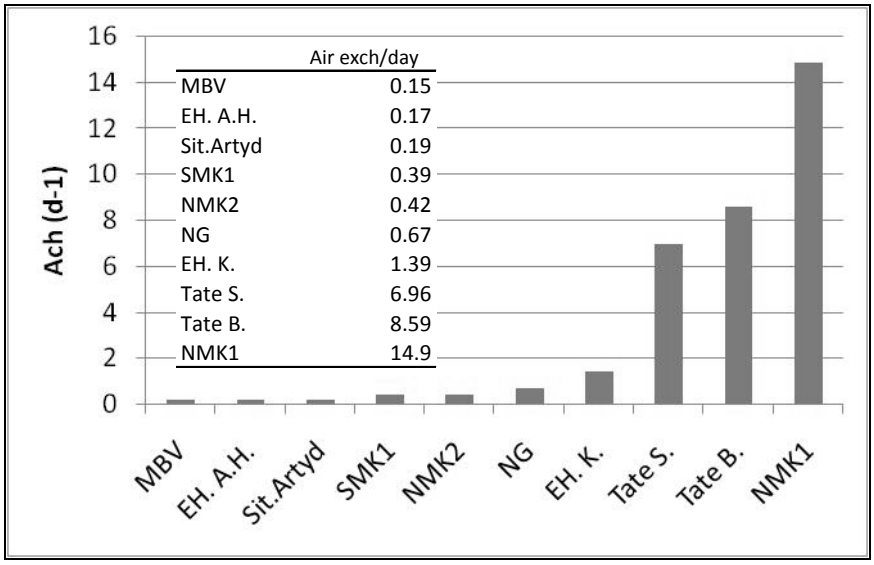


Figure 23: Air exchange rate of PROPAINT-microclimate frames. For location abbreviations see Table 3 and table in Figure text 12.

The results from all the climate measurements performed in PROPAINT are reported in Appendix 1, Table 3.

3.5.4 The dosimeter response to the environment - Dose response functions

Statistical software SPSS+ was used to perform multiple regression analysis to determine the dependence of the dosimeter responses on the environmental parameters. The statistical sample size included values of all the measurements in the museum rooms and inside the microclimate frames for all the locations shown in Table 3, except the SMK2 microclimate frame for which not all measurements were performed. Some obvious outliers from the regression fit were removed from the analysis (The lead coupons in the constructed worst case frame no 1 and one of two EWO parallels at location no. 11, GNM, Figure 14C).

Table 5 reports the environmental dose – response functions from the statistical analysis of the results from the passive gas diffusion sampling, the climate measurements and the dosimeter measurements. The dose response functions illustrate the similar sensitivity to the environment measured for pair of dosimeters (RM-PQCs and EWOs, and L-PQCs and Glass slides). NO_2 is a main environmental factor that reacts with both the EWO and RM-PQC, whereas acetic acid is the main component found to react with the Glass dosimeter (GSD) and L-PQC dosimeter (Table 5).

Table 5: Dose response equations for "PROPAINT-dosimeters". Grey shaded results are from a previous evaluation in the EU project MASTER. EWO = Early Warning Organic dosimeter. RM-PQC and L-PQC = Resin Mastic and Lead Piezoelectric Quartz Crystal dosimeters. GSD = Glass Slide Dosimeter. Gas concentrations are in µg m^{-3}, AcAc = Acetic Acid, T = Temperature (^oC) and RH = Relative Humidity (%).

Dosimeter	Dose-response eq.	R^2	Removed data
1. EWO - linear	EWO*1000 $= 3.8 + 0.55*NO_2 + 0.82*O_3$	0.66	GNM-Room (one high parallel)
2. EWO - non linear	EWO*1000 $= 3.9 + \sqrt{T}\ (0.12*NO_2 + 0.28*O_3)$	0.59	
3. EWO (EU project MASTER) Museum rooms	EWO*1000 $=8.7+\sqrt{UV}+\sqrt{T}*(0.11NO_2+0.15O_3)$	0.73	
4. EWO (EU project MASTER) Showcases	EWO*1000 $=4.5+\sqrt{T}(0.16NO_2+0.052O_3)$	0.71	
5. RM-PQC	RM-PQC $= 0.61*NO_2 + 0.24*T$	0.92[1]	SIT (but little difference +/- SIT)
6. GSD	GSD * 1000 = 0.20**AcAc	0.75[1]	
7. L-PQC	L-PQC = 7.4 + 0.017*AcAc	0.83	Tate B - Room
8. Lead Coupons	LC = 1.5*AcAc + 7.3*RH	0.83[1]	SIT

[1]For regression through the origin, the interpretation of R^2 is different and cannot be compared to R^2 for models which include an intercept.

3.6 Case studies performed in PROPAINT

Six different case studies were performed within PROPAINT:

- Dosimeter exposure in "Rubens frame" with and without painting;
- Dosimetry in microclimate frames with different Air Exchange Rate;
- Continuous monitoring in Experimental Frame;
- Dosimetry in experimental frames containing different materials;
- Dosimetry in 19th century frame in Tate Store, London, UK
- Measurements at the National Research Institute for Cultural Properties (Tokyo, Japan).

3.6.1 Summary

Major conclusions from the case studies described below were:

- Both pollutants that infiltrate form outside of the microclimate frame (NO_2) and that are emitted inside the microclimate frame (acetic acid) deposit on the painting. (Case 1).

- Lowering of the air exchange in a microclimate frame can give higher impact of gaseous pollutants on materials, inside the microclimate frame, that are sensitive to organic acids (acetic acid) being emitted inside the microclimate frame, and lower impact on materials, inside the microclimate frame, that are sensitive to oxidants that infiltrates from outside the frame. (Case 2).

- Continuous monitoring with the L-PQC can measure the build up of organic acids (acetic acid) inside a microclimate frame after closure and increases in temp and RH, as fast rate of change of the dosimeter. The stable level reached after the fast change lasting from a few days (T and RH change) to less than one month (initial change after closing) is indicative of the emission strength and acetic acid impact on sensitive materials inside the enclosure. (Case 3).

- The impact of organic acids (acetic acid) on sensitive materials inside microclimate frame can be significantly reduced by installing barrier films over emitting materials (in this case oil-tempered hardboard) and emission absorbing material inside microclimate frames. In the experiments the combination of PET covered Al-foil and charcoal cloth was found to be most effective. The use of Foamex (and no absorber) was nearly as effective. The use of Melinex and charcoal cloth and Melinex only also had a significant effect. (Case 4).

- Values for the L-PQC dosimeters after 1 month's exposure with oil-tempered hardboard (Table 7) were similar to those obtained for the test with oil-tempered hardboard covered with thin Melinex (Table 8). This implies, on basis of previous exposures and calibration, that levels of organic acids may exceed 1000 µg m^{-3}. Though the effect on paintings of levels of organic acids exceeding 1000 µg m^{-3} is still not known some corrosion of the small brass plates at the back of the frame had previously occurred. The recommendations would be; to aim to reduce the levels of emitted acids in this painting. (Case 4 and 5).

- A storeroom location at the National Research Institute for Cultural Properties, Tokyo (Japan) showed a level of photo-oxidizing impact on the EWO dosimeter slightly higher than that evaluated to be acceptable for an archive, but being acceptable for a purpose built museum. The value was lower than that measured for all but one of the museum rooms (i.e. Tate store) in the general campaign, but higher than all but two of the microclimate frames (the NMK1 Leonardo frame and MBV frame, Appendix 1). (Case 6).

The main conclusions from the separate case studies and the procedure in the studies are given below:

3.6.2 Case 1: Dosimeter exposure in "Rubens frame" with and without painting

In order to determine possible differences between microclimate frames with and without a painting installed the Lead PQC dosimeters, lead coupons, resin mastic PQC dosimeters and resin mastic strips were exposed in the "Rubens frame" located at Statens Museum for Kunst in Copenhagen with and without the painting installed.

Higher values for lead coupons in the frame without the painting installed (weight increase = 2546 mg/m^2) than with the painting installed (weight increase = 716 mg/m^2) indicated a possible reduction of organic acid deposition flux to the coupons due to net organic acid deposition on the painting.

Significantly higher values were measured for the RM PQCs inside the frame without the painting installed (f/F_0 = 11) than with the painting installed (f/F_0 = 1.8), with the same light exposures in the room in both cases. This result may be due to difference in tightness of the frames for the two situations, difference in light conditions (light levels without the painting were high) or an indication of increased deposition of NO_2 inside the frame with the painting installed. In both cases a lower value was measured inside than outside (f/F_0 = 18.8) of the microclimate frame.

The results from this case study indicates that both a pollutant that infiltrates form outside of the microclimate frame (NO_2) and a pollutant that is emitted inside the microclimate frame (acetic acid) deposit on the painting.

3.6.3 Case 2: Dosimetry in microclimate frames with different Air Exchange Rate

In order to investigate the relationship between air exchange rate and dosimetry results inside microclimate frames for paintings, an experiment with three different microclimate frames was designed. The four dosimeters (EWO dosimeter, Glass Slide dosimeter, RM-PQC and Lead coated PQC dosimeters) and lead coupons were exposed for three months inside three microclimate frames with different air exchange rate designed particularly for this experiment.

The preliminary conclusions from these exposures were:

1. A reduction in the air exchange rate of three investigated microclimate frames gave higher corrosion of lead samples located inside them, - despite covering of the internal wood surfaces with Al-foil. This may, as was shown in the PROPAINT general exposure programme, be explained with increased concentration of organic acids, and in particular acetic acid inside the frames.

2. A reduction in the air exchange rate of three investigated microclimate frames gave lower change of resin mastic on RM-PQCs and of EWO dosimeters located inside them. As the light exposure was similar inside the frames this may be explained by a decrease in infiltration of oxidizing gaseous pollutants to the inside of the microclimate frames, particularly of NO_2, as was also shown in the PROPAINT general exposure programme.

The procedure for the experiments and the results were:

Commercial box frames, with dimensions 50 cm by 41 cm by 2 cm, were modified by covering the interior wood surfaces with aluminium film fastened with self adhesive aluminium tape and the infiltration paths sealed with self adhesive aluminium tape. An aluminium back frame was added to a third frame to achieve a lower air exchange rate. The air exchange rates were measured with the carbon dioxide tracer method (Calver et al., 2005).

Air exchange rates of approximately 2.5 per day (frame A) and 1.5 per (frame C) day were achieved with the two first frames. For the third frame a lower air exchange rate of approximately 0.3 per day (frame B) was achieved. A piece of 2 mm European Oak was added to each frame.

The temperature and RH was continuously measured in each frame and the light and UV levels were continuously measured beside one of the frames. The air exchange rate was measured at the beginning and end of the exposures.

It was observed that the values for the L-PQCs, lead coupons and Glass slides correlated negatively with the air exchange rate (Table 6) where as the values for the RM-PQCs and EWOs correlated positively with the air exchange rate (Table 6). RM-PQC and EWO values are in the range expected for a microclimate frame. The L-PQC result for microclimate frames A and C are quite low where as the L-PQC value for microclimate frame B (lowest air exchange) is higher and at a level indicating some risk (Figure 15). The trend for the Glass slides is similar, but the results for location C and A indicate somewhat higher risk (one level higher in Figure 15).

Table 6: Results from measurements of dosimeters in three frames with different air exchange rate.

Microclimate frame	**Air exchange rate (d^{-1})**	**L-PQC (% change)**	**Small Pb coupons (Weight gain, mg/m^2)**	**Single large Pb coupon (Weight gain, mg/m^2)**	**Glass slide (ΔE-value)**	**RM-PQC (% change)**	**EWO**
A	2.5	5.9	629	562	0.027	7.40	0.0070
B	0.3	20.6	2896	2851	0.163	2.59	0.0034
C	1.5	6.75	1214	785	0.080	3.58	0.0062

3.6.4 Case 3: Continuous monitoring in Experimental Frame

The L-PQC dosimeter with continuous recording facilities (battery operated) was set up for testing in the experimental frame prepared in the laboratories of the National Museum in Krakow (Figure 24). The frame had the following dimensions: 65 cm x 59 cm x 9.4 cm

(Volume of frame: is 0.036 m^3). The air exchange rate of the frame was about 1.3 per day. A piece of lime wood was placed inside the frame: 47,7 cm x 53,2 cm x 2 cm = 0.0051 m^3.

The main conclusions from the exposures were:
1. The initial rate of change of the L-PQC during the first about 5 – 20 days is fast when enclosed and exposed to untreated wood in a low air exchange microclimate frame. The rate of change is then levelling off to a slow rate of change. This can be explained with the building up of organic acids (in particular acetic acid) inside the microclimate frame after it is closed.
2. The total change of the L-PQC over a longer period seems to depend much on the total initial change (point 1), which may be explained by the total emission strength of the sources (wood) inside the microclimate frames.
3. Increase in temperature and RH caused a further fast rate of change over 2 - 3 days to a stable response level.

For the L-PQCs it seems that an exposure time of about 30 days may be sufficient to compare the inside impact of acetic acid (combined with temperature and RH) in microclimate frames. The continuous measurement with the L-PQC may, in addition, make possible an evaluation of the rate of build up of the pollutant exposure inside the frame and also of increases in temperature and RH that increases the impact.

The properties of the experiment, microclimate frame and the result are further described as follows:
The frame inside was secured using Aluminium foil 3M (nr 425) and it had a poly-carbonate back plate. Temperature, RH, pressure, CO_2, acoustic emission and dimension sensors were also included. The frame was placed into a microclimate chamber. The strong increase in the rate of change of the L-PQC was observed after about 5 and 7 days lasting for about 5 and 15 days respectively (black and green curves in Figure 24). The total change over this period was about 12 % (Which was higher than the value (6.75 %) obtained for the English Heritage frame C (Case 2) with a similar air exchange rate and piece of oak wood (80 g) enclosed, after exposure for 3 months). After about 20 days an increase in temperature and RH seemed to cause a further change in the crystals (up to 20%) which remained a steady level despite further changes in RH and T.

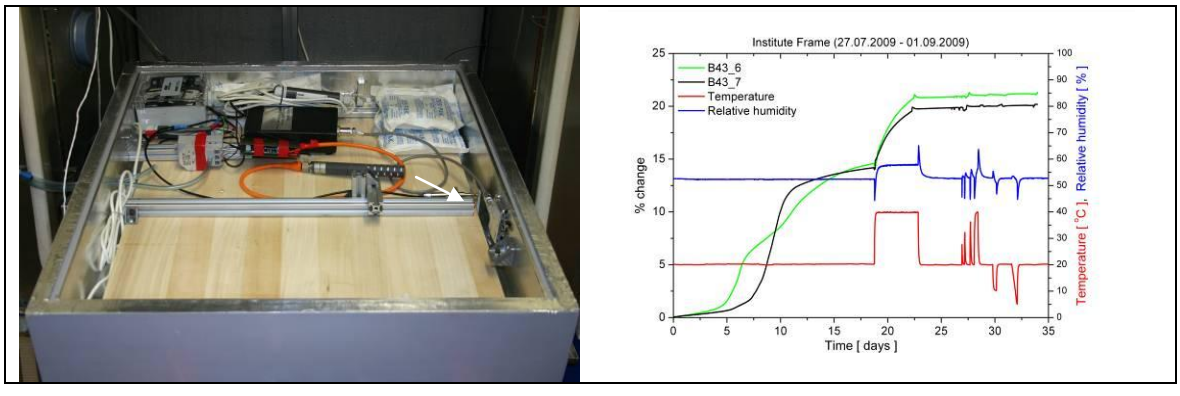


Figure 24: The position of the L-PQC dosimeter (crystals in flat silver holder) is shown using the arrow (left). The green and black traces show the change (%) in the crystals on exposure. The change occurs over the first 10/15 days. After 20 days the conditions in the microclimate chamber were changed (RH,T) (Right).

3.6.5 Case 4: Dosimetry in experimental frames containing different materials

Measurements with L-PQC dosimeters were performed within experimental microclimate frames in Tate Store, London, to assess the effect of different methods to mitigate impact from acid emission from oil-tempered hardboard inside the microclimate frames.

The main conclusions are given by Table 7 which ranks the microclimate frames from the one with the lowest (1) to the one with the highest (5) impact on the L-PQC from organic acid emitted inside the frame.

Table 7: Results for one month exposure of the L-PQC dosimeters in microclimate frames using oil tempered hardboard and different modifications to mitigate organic acid impact.

Ranking	**Frame**	**Average (% change)**	**Parallels (% change)**
1	Oil-tempered hardboard, polyethylene terephthalate (PET-covered Aluminium), and charcoal cloth.	1.8	1.13, 2.5
2	Oil-tempered hardboard and Foamex	4.1	3.3, 4.8
3	Oil-tempered hardboard, thin Melinex, and charcoal cloth	12.6	15.6, 9.5
4	Oil-tempered hardboard with thin Melinex	13.4	10.8,15.9
5	Oil-tempered hardwood (normal practice)	24.2	25.6, 22.7

The test frames (Table 7) were prepared using the oil-tempered hardboard that is currently in use at the Tate. Oil-tempered hardboard is the most rigid/protective material and is therefore best for larger works. Foamex board, for example, may emit less than oil-tempered hardboard, but it is also less rigid/protective and hence not suitable for large works. One frame was left to represent normal practice and others were modified, as described in Table 7, with the addition of materials for reducing any organic volatile acids emitted from the oil-tempered hardboard.

Two PQC lead coated crystals were used in each frame. They were clamped in a steel support (Figure 25). Lead coupons and A-D strips were also mounted inside the frames (Figure 25). Measurements of levels of organic acids (acetic and formic) were also made using diffuse passive samplers.

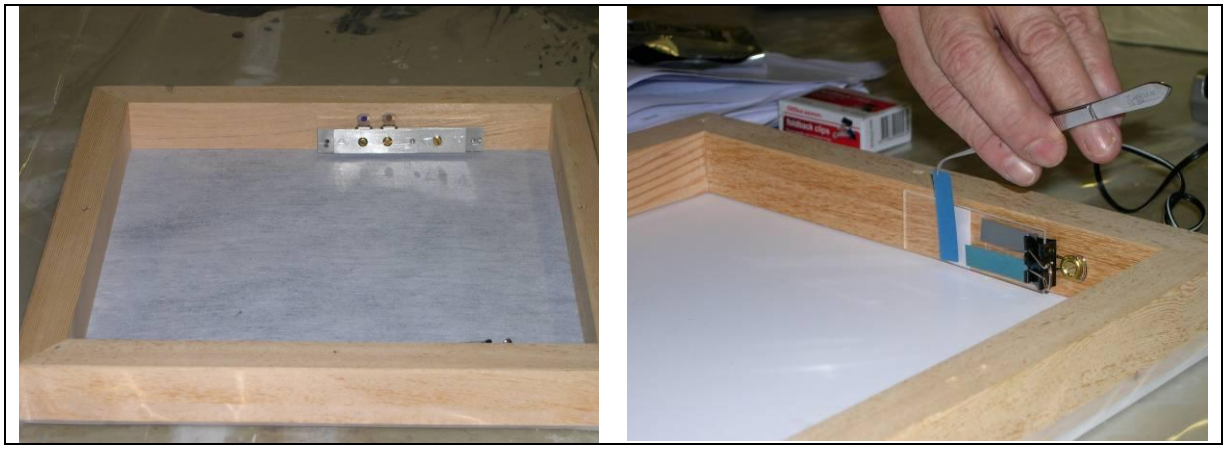


Figure 25: Two lead coated PQC crystals were clamped in a steel support and fastened to one end of Frame no.2 containing Foamex (Left). Lead coupons and A-D strips were also mounted inside the frames (Right). Comparison was made between colour of unexposed strip held in tweezers and exposed strip for Frame no.2.

Preliminary conclusions show that the values obtained from the change in the crystal coating follow the values obtained for the organic acids from the passive sampling, i.e. where values are higher, and then the crystal response is higher. The colour change in the A-D strips compared favourably with expected colours (read from the colour chart provided by the manufacturers) from the measured levels of acetic acid. Since the exposure was performed within the frames (in the dark) there was no additional contribution from the light.

3.6.6 Case 5: Dosimetry in 19th century frame in Tate Store

In this Case Study two L-PQC crystals, a lead coupon, and an A-D strip were placed at the back of a wooden frame with oil-tempered hardboard back which was covered with thin Melinex. The painting inside the microclimate frame was Dante Gabriel Rossetti's painting "Sancta Lilias" (Tate Store, acquisition no. N02440, oil on canvas 483 x 457 mm frame: 815 x 795 x 105 mm) (Figure 26). Table 8 gives the results from the L-PQCs.

Table 8: Exposure of L-PQC in the back of the frame of Rossetti's painting.

Exposures	**Average (% change)**	**Parallels (% change)**
Rossetti (1st exp) (1month)	23.5	22.2, 24.8
Rossetti (2nd exp) 50 days	28.7	27.6, 29.8

Figure 26: Back of Rossetti painting with hardboard backing removed. Top right hand corner shows crystals mounted in steel frame and top left corner shows lead coupon and A-D strip (Left). Reverse of Rossetti painting showing deposits on brass plates (Right).

3.6.7 Case 6: Measurements at the National Research Institute for Cultural Properties (Tokyo, Japan)

The EWO, PQC and the Glass slide dosimeters were exposed in the store room of the National Research Institute for Cultural Properties, Tokyo (Japan) from June to September 2009 (Figure 27, Table 9) along with objects such as oil paintings and Japanese Lacquer boxes (urushi ware). The climate conditions during the exposure were relative humidity between 55 and 60 % and temperature between 24 and 26 ºC.

Figure 27: Dosimeters exposed in store room of the National Research Institute for Cultural Properties, Tokyo, Japan.

Table 9: Results from dosimeter exposures in the National Research Institute for Cultural Properties, Tokyo (Japan).

Location	EWO Dosimeter (abs. Units)	L-PQC (% change)	Lead Coupons (weight increase mg/m^2)	Glass slide (ΔE–value)
Store Room	0.0095	3	340	0.031

The results from EWO and L-PQC dosimeters, and the lead coupons are given in Table 9 and Figure 28. They indicate that the environment in the store room is acceptable for a purpose built museum concerning photo-oxidizing effects and good regarding potential organic acid impacts (Figure 15).

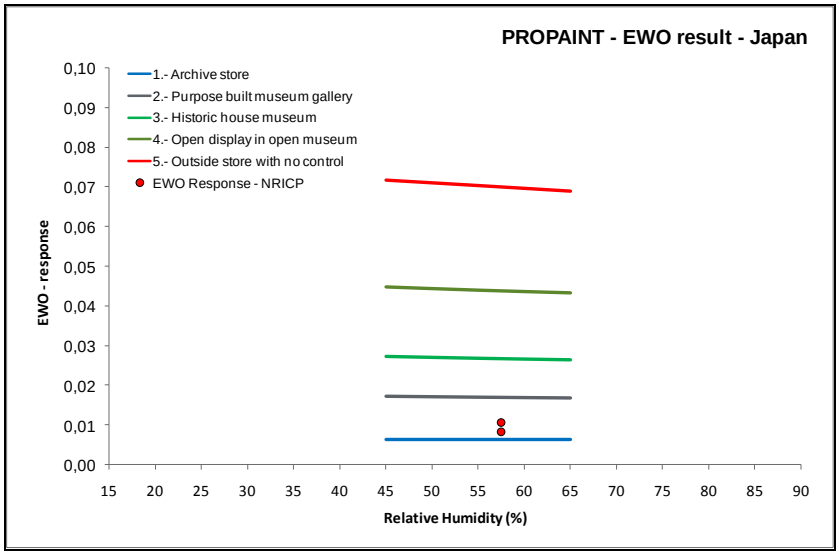


Figure 28: EWO results at the National Research Institute for Cultural Properties, Tokyo, Japan.

4 Degradation of varnishes due to the environment

4.1 Summary

The results of the current study of varnishes, natural and synthetic, have provided information for the first time about the ageing of varnishes exposed to known levels of inorganic and organic pollutants. The natural resins, resin mastic and dammar, were found to be sensitive to the oxidising agents NO_2, ozone and acetic acid, and there was some dependence on RH. In comparison, the synthetic resins, MS2A and B72, on the whole showed less sensitivity to these pollutants. B72, however, did exhibit marked sensitivity to ozone, and this was shown to be RH dependent; ozone was found to be more aggressive at low values of RH than at high RH values. Where Tinuvin 292 was used, as in dammar and MS2A, its retarding action on degradation was confirmed. Markers of change at the molecular and macro-levels were identified and then used to rank the physico-chemical changes that were measured following the exposure within microclimate frames and in rooms in selected museums. Differences were observed between varnishes exposed within microclimate frames and in rooms for each location, which could not be attributed to light and were found to be influenced by levels of acetic acid within the microclimate frames and their measured air exchange rates.

One of the important objectives of the PROPAINT project was to investigate the quality and protective effect of varnishes used as remediation treatment for paintings when exposed to pollutant and climatic factors generally, and in microclimate frames particularly. To this aim the following aspects were investigated:

- The degradation of paint varnishes occurring as a result of exposure to pollutant and climatic factors;
- Exposure of paint varnishes inside and outside microclimate frames and assessment of the degradation effect of the microclimate generated within the frames.

Based on a literature survey the investigation was performed on dammar, mastic, MS2A and Paraloid B72 resins, with the addition of Tinuvin 292 in dammar and MS2A. Several varnish samples were prepared as described in Chapter 4.3. One part of the varnish samples were subsequently subjected to accelerated ageing to the pollutants NO_2, O_3 and acetic acid at different values of relative humidity (Chapter 5.3). The PROPAINT project has undertaken for the first time a systematic investigation of the effect of various pollutants and climate conditions on the physico-chemical composition of the selected resins. The remainder of the varnish samples were exposed in various museum environments and subjected to natural ageing for exposure times between nine months and 1.5 years.

The techniques that were used to determine the physico-chemical changes and modifications in the paint varnishes as an effect of the natural and artificial ageing were: Dynamic Mechanical Thermal Analysis, Matrix Assisted Laser Desorption Ionization-Mass Spectrometry, Optical Microscopy, Scanning Probe Techniques [Atomic Force Microscopy and Micro-Thermal Analysis], Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS), Gas Chromatography/Mass Spectrometry (GC/MS). Chapter 4.4 and 4.5 summarise the most significant results obtained during the PROPAINT project.

4.2 Implications for preventive conservation

The PROPAINT project for the first time focussed on the effect of some pollutants on the degradation of natural and synthetic resins. It was possible to determine that the investigated pollutants, NO_2, O_3 and acetic acid, do have an effect on the degradation of natural resins, and a lesser effect on the synthetic resins. This indicates that light is not the only factor that must be taken into account to for the long term preservation of paintings. In addition it should not necessarily be assumed that the exposure situation within microclimate frames is better than that outside of microclimate frames. Results showed that, where air exchange rates were low and significant levels of acetic acid were measured (c. 1000 µg m^{-3}), then measurable alterations occurred in the varnishes.

There is considerable interest in the effect of pollutants on organic materials as only a limited amount of information exists. Studies of pollutant effects on parchment have been made in the IDAP project (Larsen, 2007), and studies of pollutant effects on resin mastic varnish were performed in the MIMIC project (Odlyha, 2007). Mass Spectroscopy (MS) studies of natural ageing and of light ageing of resin mastic have been performed. In these studies it was demonstrated that the ageing results in addition of oxygen to the resin compounds, with simultaneous abstraction of hydrogen (Dieteman et al., 2001).

Studies of light ageing and NO_2 ageing of resin mastic were also performed in the MIMIC project. The information was used to calibrate the response of resin mastic coated crystals to NO_2. MS studies also demonstrated that controlled light induced deterioration of mastic coatings on Piezoelectric quartz crystals (PQCs, as used in PROPAINT, Chapter 4) was accompanied by systematic changes in the crystal frequency (Cavicchioli, 1996). This showed that resin mastic coated strips could be used as dosimeters in preventive conservation practice. The MIMIC project demonstrated that the evaluation of the change in the strips could be performed by using Reflectance FTIR (Odlyha, 2005).

The results from the exposures of varnishes in microclimate frames and museum rooms showed that the air exchange rate (AER) is a valuable parameter for evaluating the performance of the microclimate frames. Frames with low AERs have the advantage that they provide buffering against external fluctuations in relative humidity (RH) and temperature (T). This could help to reduce the impact of acetic acid (found to be most damaging at higher RH) and ozone (found to be most damaging at low RH) as well as limiting the ingress of oxidising pollutants. However, low AER values may provide problems: (1) Where solvent molecules are still trapped within the varnish this might lead to damages to the paint layers underneath (2) Where there are high emissions of acetic acid this would also affect the varnishes. Results have shown that acetic acid has an effect on varnishes, both natural and synthetic. High air exchange rates give better protection against the latter two effects. However, in microclimate frames with air exchange rates located in uncontrolled environments, ingress of oxidising agents and loss of climate buffering (RH and T) can cause damage to varnishes.

Although none of the varnish samples artificially and naturally aged in PROPAINT showed visible damages, cross linking and oxidation were evidenced in all cases.

The research performed in the PROPAINT project revealed for the first time the detailed chemical composition of MS2A resin, highlighting the effect of artificial and natural ageing on the physical-chemical properties of the resin, - also when Tinuvin 292 was added as stabiliser. Detailed results will be published in a paper which is under preparation.

Finally the research performed during the PROPAINT project highlighted a fundamental aspect related to the composition of paint varnishes: solvents can be trapped for very long time in the varnish layer. This was the case of the MS2A varnishes, in which the aromatic components of the solvent used for the varnish preparation were retained in the varnish film, even two years after the preparation. This tells us that care must be taken in the choice of the solvent for a varnish. - Aromatic compounds, that are known to be dangerous for the human health, can be retained in the varnish film. Their occurrence in the varnishes applied on a real painting could be harmful for the paint layers, because the aromatic compounds could migrate towards the paint films and act as solvents for some of the paint constitutes. This would have an effect on the stability of the paint layers, and it cannot be excluded that this could contribute to the well known phenomenon of the ghost images.

The PROPAINT project investigated a selection of natural and synthetic varnishes. This must be regarded as a starting point towards a detailed investigation of the response of the paint materials in the whole paint system towards the environment pollutants. Other pollutants need to be investigated as well as other paint materials. A fundamental outcome of the investigations described in this chapter is that organic materials are very sensitive to exposure to both inorganic and organic pollutants. This was observed for some paint varnishes, and it can be expected for other organic paint materials. Moreover, damage to the varnish on a painting due to environmental pollutants will increase the need to remove the damaged varnish and re-varnish the painting. This process poses additional risk to the painting itself. It is widely known that the process of re-varnishing is extremely invasive for the paint layer and its use should be reduced to a minimum.

4.3 Preparation, accelerated ageing and field exposures of varnish samples

4.3.1 Preparation

A large number of samples of a series of test strips with 6 different varnish types on steel foil were produced. The varnishes were prepared in solutions according to recipes suggested by the supplier (Kremer Pigmente, Hauptstrasse 41, 88317 Aichstetten, Germany):

1. Mastic in ethyl alcohol, 20 % w/w: 100 g mastic resin to 400 g ethyl alcohol.
2. Dammar in Shellsol A, 40 % w/w: 100 g dammar resin to 150 g Shellsol A.
3. Dammar + 2 %Tinuvin 292 in Shellsol A, 40% w/w: 2 g Tinuvin to 98 g dammar resin to 150 g Shellsol A.
4. MS2A in Shellsol A, 30 % w/w: 100 g MS2A resin to 233 g Shellsol A.
5. MS2A + 2 % Tinuvin 292 in Shellsol A, 30 % w/w: 2 g Tinuvin to 98 g MS2A resin to 233 g Shellsol A.
6. Paraloid B 72 in buthylacetate 15 % w/w: 100 g Paraloid B 72 resin to 567 g buthyl acetate.

All the raw resins were sent to the partner DCCI, to test the purity of the materials. 200 ml of each resin sample was also sent to the Birkbeck College for analysis/tests. 45 sets of the 6 different varnished steel foil samples with dimension 0.01 x 2 x 8 cm were cut from larger steel sheets prepared with the varnish using a spray gun. Before cutting, the varnished steel sheets were cured for 4 days at room temperature and subsequently for one month at 40^{o}C and 50% RH (large steel sheets) or 23^{o}C and 50% RH (smaller steel sheets kept as back up in a refrigerator at The School of Conservation in Copenhagen).
The sets of 6 different varnished samples, each single sample wrapped in acid free paper, were put into air tight Al envelopes and distributed to the exposure locations:

NILU – Norwegian Institute for Air Research, Oslo (30 sets)
University of Pisa (2 sets)
Birkbeck College, London (2 sets)
The National Museum in Krakow (2 sets)
Tate Britain, London (2 sets)
Museo de Bellas Artes de Valencia (2 sets)
Statens Museum for Kunst, Copenhagen (2 sets)
Galleria degli Uffizi, Firenze (2 sets)
The School of Conservation, Copenhagen (1set)

The dates for the different stages in the manufacture of the varnish samples were:
14th of August 2007: Preparation of varnish solutions.
21st of September 2007: Varnishing of steel sheets, left to settle.
24th of September 2007: Steel sheets placed in acclimatized oven.
24th of October 2007: Steel sheets cut into strips.
26th of October 2007: Strips sorted and packed in sets of 6 in envelopes.
29th of October 2007: Envelopes sent to recipients.

Figure 29 shows the preparation of the varnish samples.

Figure 29: Above: preparation of the varnish samples. Below: envelope containing a set of varnish samples.

4.3.2 Accelerated ageing

Accelerated ageing of the varnish samples were carried out in the exposure chambers at NILU (Figure 30).

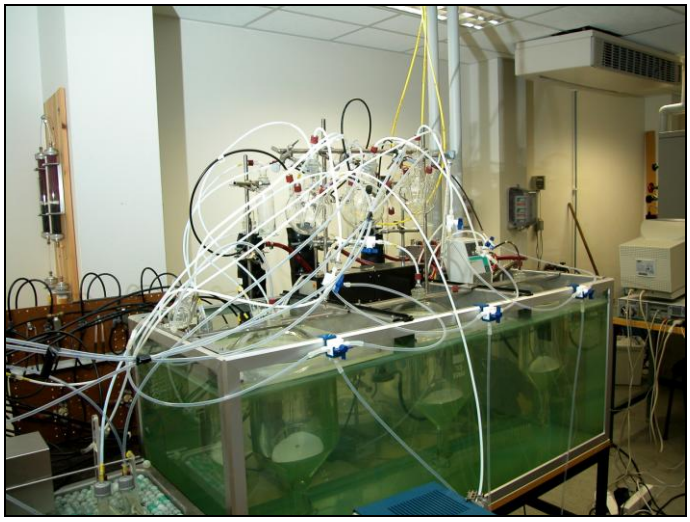


Figure 30: The exposure chambers at NILU.

The varnish samples were exposed to different pollutant and climate doses to provoke degradation effects in the varnishes. The doses were equivalent to the doses varnishes on paintings would be exposed to over long time in the environments inside and outside of microclimate frames in museums.

The source for NO_2 was permeation tubes. The source for acetic acid was a vial filled with liquid acetic acid. The average concentration of both NO_2 and acetic acid in the chamber during one exposure experiment was estimated from the weight loss of the tubes/vial, the constant air flow rate through the chamber and the exposure time. The gas source for the exposures with ozone was a UV – O_3 generator (TE Instruments ozone generator model 165). The O_3 concentration in the chamber was continuously monitored by a photometric O_3 analyzer (API, model 400). From the NO_2 + O_3 exposure it was found that the value for the NO_2 concentration includes 10 – 15 % NO_2 from NO measured as reduction in O_3 from before to after the mixing chamber.

Table 10 gives an overview of the accelerated ageing experiments carried out. Different flow rates (0.5 to 2 cm s^{-1}) and duration of the exposures were used to obtain the desired ranges of pollutants doses.

Table 10: Accelerated ageing exposures carried out at NILU with different pollutants and values for relative humidity. C (Ch) = average concentration in the chamber. t = duration of exposure. The number in brackets for the exposure 21, with a combination of NO_2 and O_3, represents the concentration of O_3.

#	Pollutant	T (°C)	Exposure period (From/To)	RH (%)	C (Ch) ppm	T (days)	Dose ppm day	Sample name BIRKBERK	Sample name DCCI
1	NO_2	22	17.12.2007 to 7.12.2007	20	5.52	10	55.19	1A	NO2-20-55
2	NO_2	22	17.12.2007 to 27.12.2007	20	13.90	10	139.03	1B	NO2-20-139
3	NO_2	22	17.12.2007 to 27.12.2007	20	21.28	10	212.81	1C	NO2-20-212
4	NO_2	22	14.04.2008 to 05.05.2008	20	11.03	21	231.56	14.4.8	NO2-20-231
5	NO_2	22	27.12.2007 to 08.01.2008	50	5.51	10	55.06	2A	NO2-50-55
6	NO_2	22	27.12.2007 to 08.01.2008	50	14.65	10	146.46	2B	NO2-50-146
7	NO_2	22	27.12.2007 to 08.01.2008	50	16.96	10	169.63	2C	NO2-50-169
8	NO_2	22	29.01.2008 to 18.02.2008	50	21.17	20	423.42	5B	NO2-50-423
9	NO_2	22	29.01.2008 to 18.02.2008	50	21.32	20	426.41	5C	NO2-50-426
10	NO_2	22	08.01.2008 to 18.01.2008	80	5.46	10	54.56	3A	NO2-80-54
11	NO_2	22	08.01.2008 to 18.01.2008	80	12.03	10	120.29	3C	NO2-80-120
12	NO_2	22	08.01.2008 to 18.01.2008	80	13.59	10	135.91	3B	NO2-80-135
13	NO_2	22	19.01.2008 to 10.03.2008	80	14.66	20	293.21	6.2C	NO2-80-293
14	NO_2	22	13.03.2008 to 11.04.2008	80	20.67	29	599.37	7.1B	NO2-80-599
15	O_3	22	14.04.2008 to 14.05.2008	20	4.35	27	117.38	8.2	O3-20-117
16	O_3	22	16.05.2008 to 16.06.2008	50	4.30	31	133.23	10.2	O3-50-133
17	O_3	22	13.03.2008 to 11.04.2008	80	3.97	29	115.13	7.2	O3-80-133
18	Acetic Acid	22	14.05.2008 to 02.05.2008	20	1.12	19	21.24	10.1	AcA-20-21
19	Acetic Acid	22	29.04.2008 to 13.05.2008	50	1,56	15	30.94	19	AcA-50-31
20	Acetic Acid	22	11.04.2008 to 28.04.2008	80	2,06	17	26.52	20	AcA-80-26
21	$NO_2 + O_3$	22	19.01.2008 to 29.02.2008	50	5.81 (1.27)	10		6.1	(NO2+O3)-50-(50+10)

Exposure of 2 sets of the 6 different PROPAINT varnish samples to concentrations of 100 % (glacial) acetic acid vapour, giving a calculated concentration of $4.4*10^4$ µg/l, for periods of 1.5 and 3 months were performed.

4.3.3 Field exposures

Ten sets of prepared samples of the different varnishes were distributed to five end-user museums for the field test. The samples were mounted both inside and outside of microclimate frames for paintings and showcases (Uffizi) for long exposure time to evaluate the protective effect of the microclimate frame on the varnish ageing. Table 11 reports the exposure sites and durations.

Table 11: Sites and durations for field exposures of varnish samples in PROPAINT.

Site	Time	Brake in exposure	Total duration (weeks)
Tate Britain, London (UK)	November 2007 to April 2009	1st Feb. 2008 to 24st Oct. 2008	38
Statens Museum for Kunst, Copenhagen (DK)	November 2007 to March 2009		70
Museo de Bellas Artes de Valencia (ES)	November 2007 to March 2009	March 2008 to June 2008	56
National Museum in Krakow (PL) "Leonardo"	December 2007 to March 2009		66
National Museum in Krakow (PL) "New microclimate frame"	January 2008 to March 2009		62
Uffizi Gallery. Florence (IT)	November 2007 to May 2009		75

Figure 31 to Figure 36 show the exposure sites, also explaining if the varnish samples were exposed in the darkness or in the light.

Figure 31: Tate Britain, London (UK). Inside the frame. The varnish samples are exposed to light. No photos are available from outside the frame; - they were exposed to light.

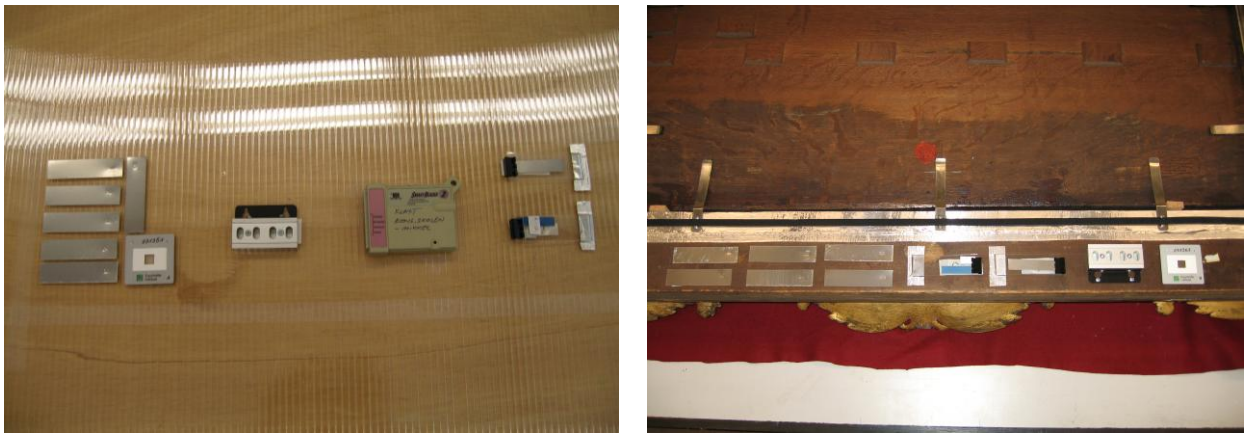


Figure 32: Statens Museum for Kunst, Copenhagen (DK): Inside (left) and outside (right) the frame. The varnish samples are exposed in the darkness.

Figure 33: Museo de Bellas Artes de Valencia (ES). Inside (left) and outside (right) of the frame. The varnish samples were exposed in the darkness.

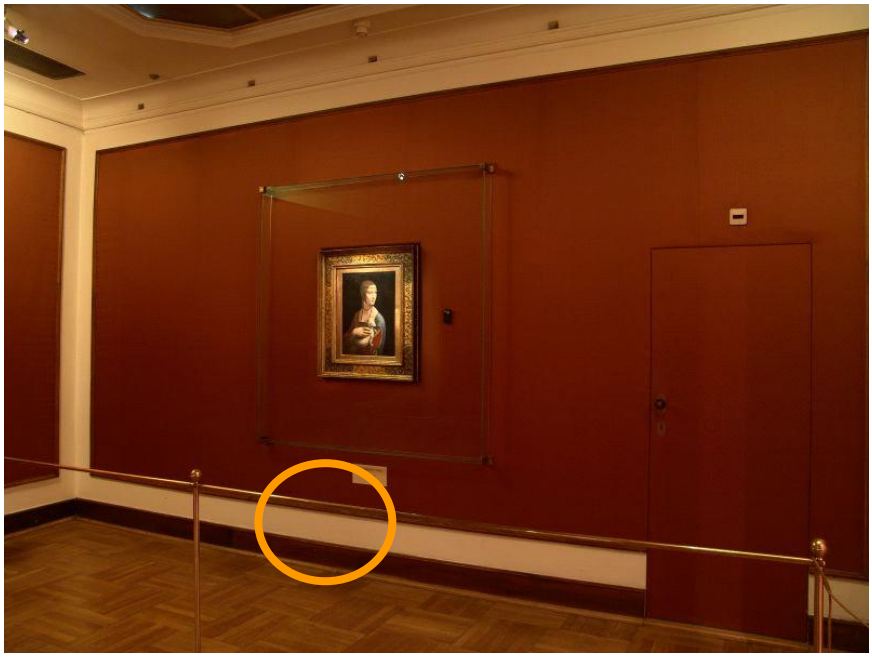


Figure 34: National Museum in Krakow (PL) "Leonardo". The varnish samples are exposed to light.

Figure 35: National Museum in Krakow (PL) "New microclimate frame". The varnish samples are exposed in the darkness.

Figure 36: Uffizi Gallery. Florence (IT). Inside (left) and outside (right) the showcase. The varnish samples are exposed to light.

4.4 Analytical investigations- molecular aspects

In this chapter the main results on the molecular analyses on the natural and synthetic resins are presented. Materials and methods used are reported in the Appendix 1, and detailed analytical data will be presented in a publication which is under preparation.

4.4.1 Natural resins

The analysis of the natural resins mastic and dammar were performed by means of GC-MS. The use of Gas Chromatography - Mass Spectrometry permits the evaluation of the molecular composition of the soluble low molecular weight components of the resins. The samples were extracted in a suitable solvent and injected into the GC-MS. The mixture of the soluble low molecular weight components (which in the case of dammar and mastic are triterpenoids) are separated in the GC column and revealed by the MS system. The resulting diagram, which is called a "chromatogram" is characterised by peaks, each of which represents a specific molecular component. The area of the peak is proportional to the amount of the component that generated it (for more details see Pinna et al, 2009).

By evaluating the nature of the molecules present it is possible to evaluate the oxidation state of the resin. This allows us to determine if the resin has been oxidised by the environment and the pollutants. By evaluating the abundance of the peaks obtained from a weighed amount of the resin, it is possible to evaluate the amount of low molecular weight components that can be extracted from the resin. This is a measure of the cross linking reactions that take place in a resin and that causes loss of solubility which is observed with time in an aged resin film. By comparing the molecular composition and the amount of soluble components that are obtained after artificial and natural ageing with that of the fresh resin it is possible to determine the change in the resin composition, and possibly how this is determined by the pollutants and environmental parameters.

4.4.1.1 Effect of pollutants on the oxidation and loss of solubility of the resin.

NO_2, O_3 and acetic acid are oxidants that act on the resin molecular composition by oxidising its components. In most cases the dose is a key factor in determining the degree of oxidation. Acetic acid was observed to be very efficient in oxidising the natural resins, even in

comparison to the inorganic gases NO_2 and O_3. These pollutants are also responsible of the resin loss of solubility due to cross linking phenomena, as highlighted in the figures below, where the observed amount of free triterpenoids is reported versus ageing (Figure 37 and Figure 38). The diagrams clearly show that natural ageing plays an important role in the loss of solubility of the natural resins. Figure 38: also shows how Tinuvin 292 slows down the loss of solubility of dammar resin.

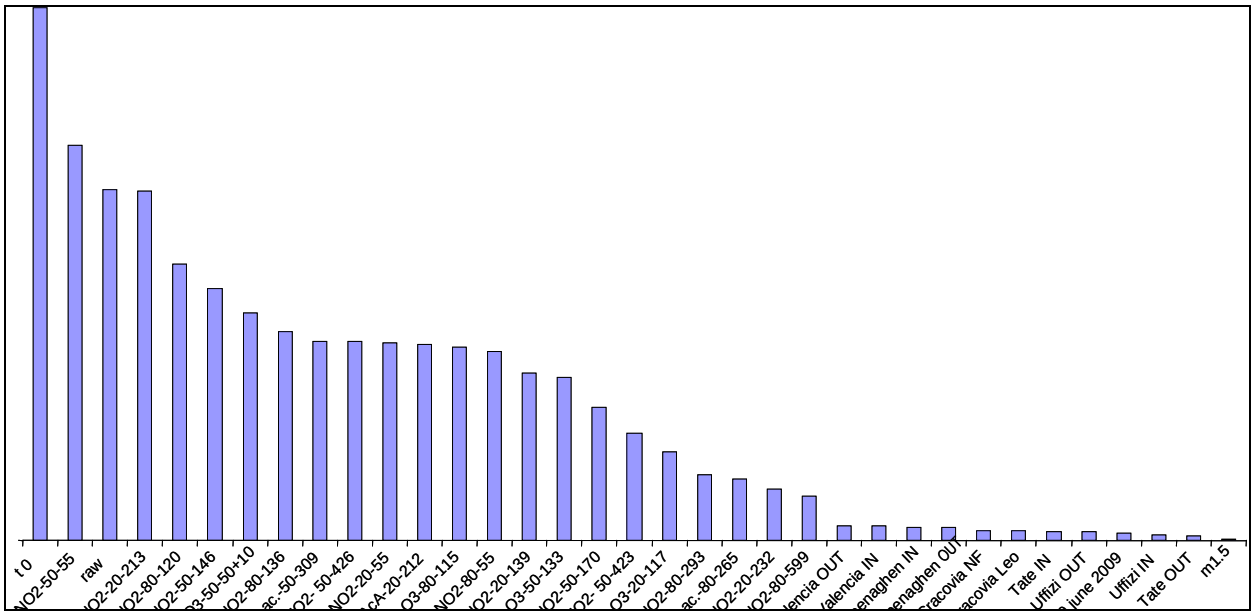


Figure 37: Amount of free triterpenoids in mastic resin after ageing, for the different ageing regimes (Table 10).

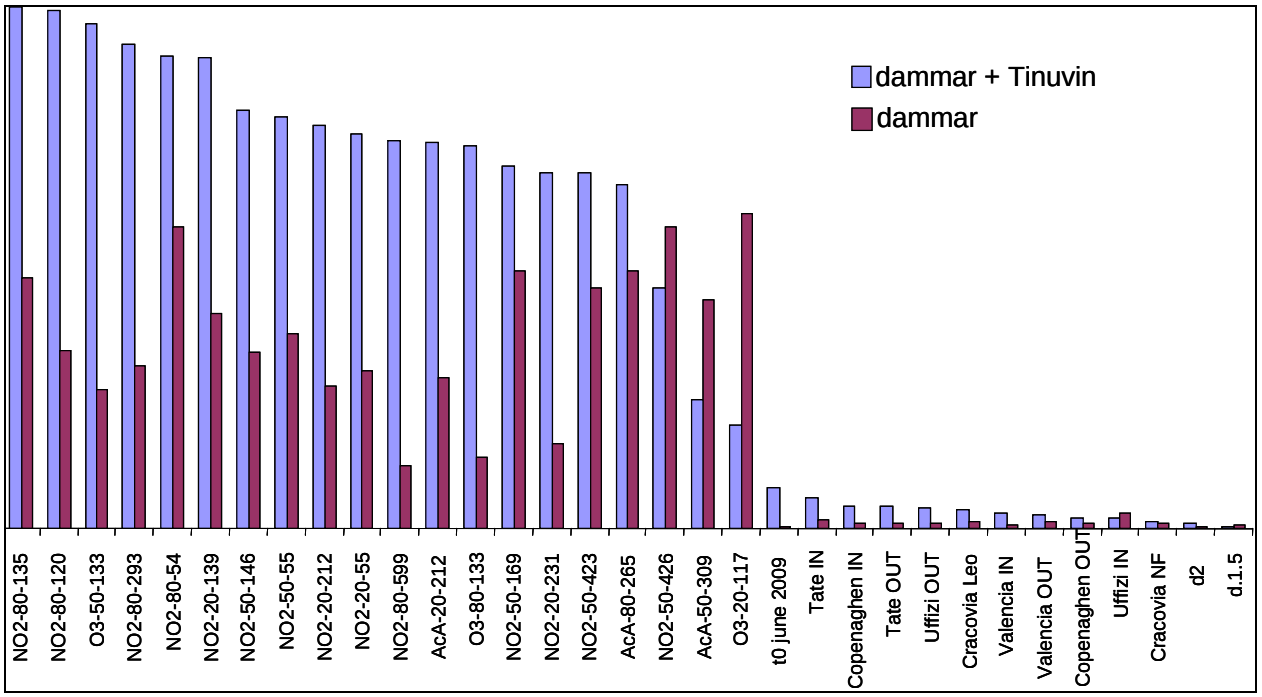


Figure 38: Amount of free triterpenoids in dammar resin after ageing, for the different ageing regimes (Table 10), with and without Tinuvin 292.

4.4.1.2 Effect of the protective effect of microclimate frames against oxidation and loss of solubility of the resin

The analysis of varnish samples exposed with paintings (outside and inside of microclimate frames) in museum environments revealed that the oxidation and solubility state of the varnishes is not the same in all locations, and differences were observed between those samples that were exposed inside and those outside the frames. It is however important to stress that no systematic trends are observed. For example, the solubility of dammar, dammar + Tinuvin 292 and mastic resin seem to be affected differently when exposed to the same museum conditions, as highlighted in Figure 39. The different behaviour cannot thus be ascribed to the different environmental conditions only, but also to the different physicochemical reactivity of the different resins with respect to light, RH and pollutants.

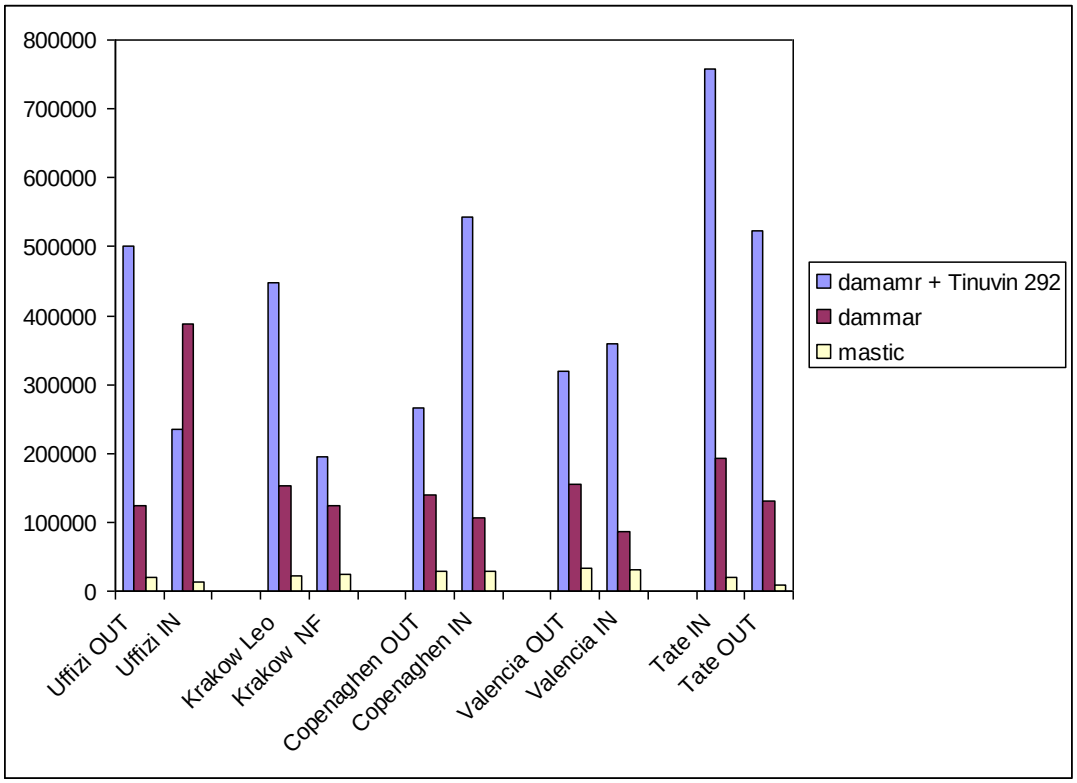


Figure 39: Amount of free terpenoids extracted from the natural varnish samples that were exposed on site, inside and outside the frames.

4.4.2 Synthetic resins

The analysis of synthetic resins was performed by means of thermal desorption and/or pyrolysis mass spectrometry. Pyrolysis was used to analyse the polymeric fraction of the two synthetic materials (Paraloid B72 and MS2A). Thermal desorption permits to obtain information on the low molecular weight fraction of the synthetic materials, without subjecting them to any analytical pre-treatments.

4.4.2.1 Paraloid B72

Pyrolysis of Paraloid B72 has been extensively studied: It is known that, under pyrolysis the resin undergoes depolimerisation, known as unzipping, giving rise to, as the main pyrolysis product, the formation of its monomers; methyl acrylate and methyl metachrylate (Sobeih,

2008). Pyrolysis of Paraloid B72 was performed at 600°C. The resulting pyrogram (Figure 40), shows three main regions; that of monomers, that of dimers and that of sesquimers.

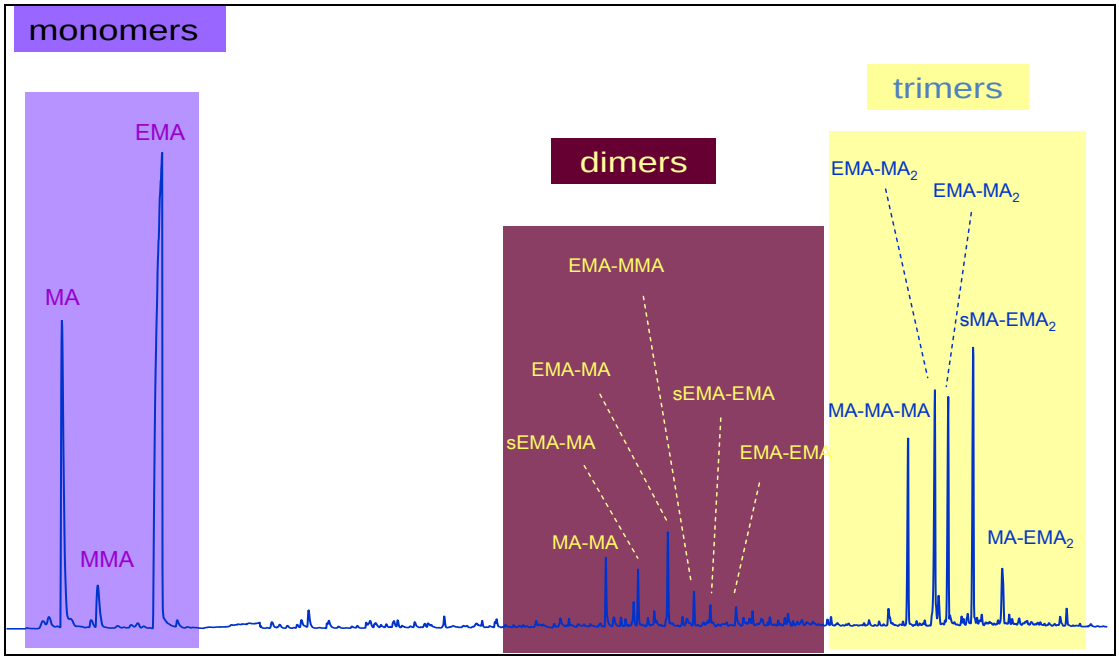


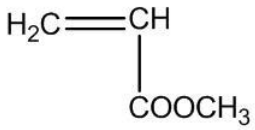
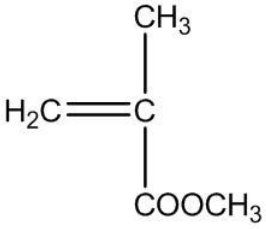
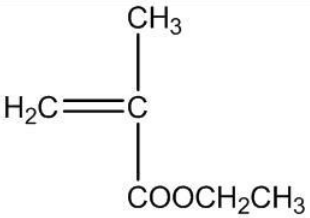
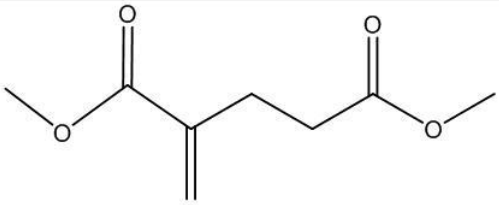
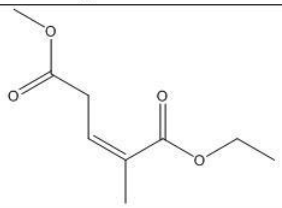
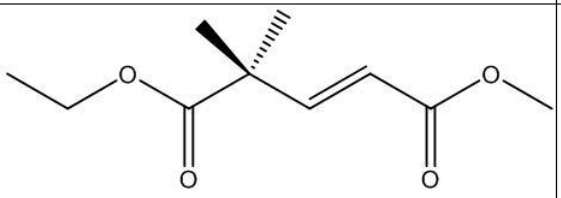
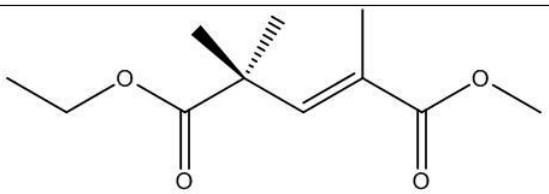
Figure 40: Pyrogram of Paraloid B72 at 600°C.

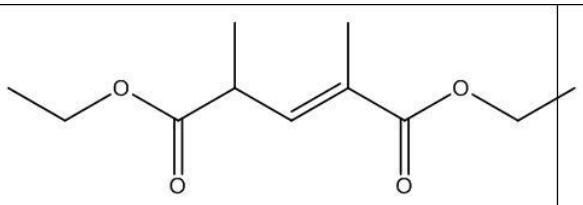
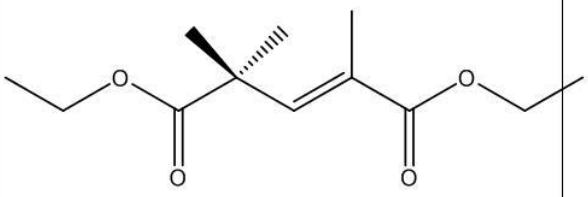
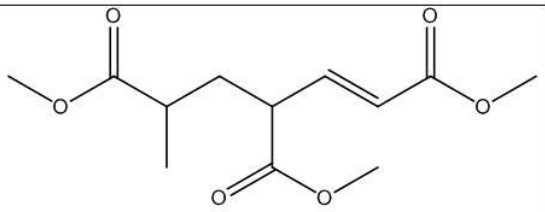
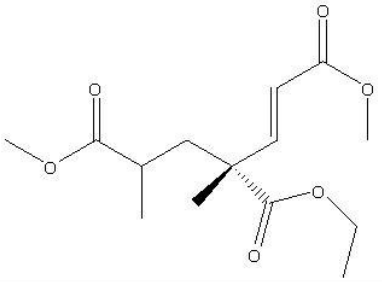
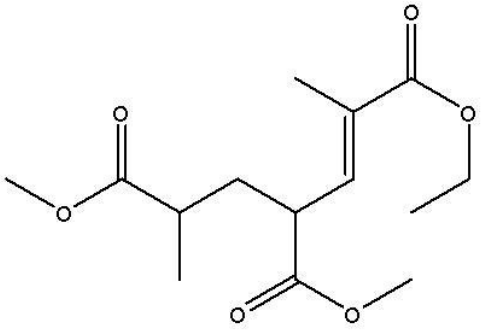
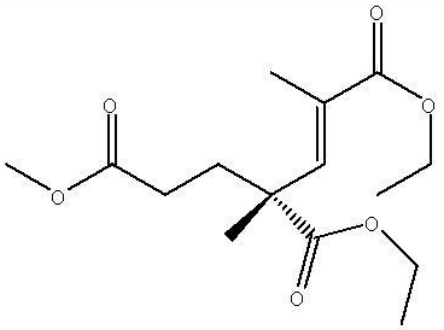
The main peaks identified in the chromatogram are listed in Table 12 together with molecular weights and molecular structures. For the dimers, sesquimers and trimers, the assignment of the molecular structure is suggested on the basis of the interpretation of the mass spectra.

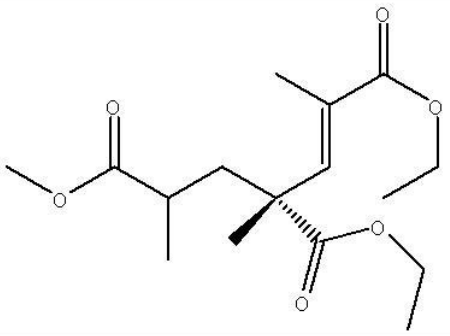
The analysis of the samples, subjected to both natural and artificial ageing, showed extremely reproducible chromatograms, suggesting the high stability of the resin to oxidation. From the pyrolysis performed at 600°C, it is not possible to draw any conclusions about modification of the resin solubility, or about the occurrence of cross linking phenomena and changes of other physical properties.

The samples were also subject to thermal desorption at 70 °C to evaluate if volatile low molecular weight molecules were produced by the resin degradation, but such low molecular weight molecules were never observed.

Table 12: Compounds identified in pyrolysis of raw Paraloid B72, molecular weight and molecular structure. The symbols correspond to those reported in the chromatogram in Figure 40.

Symbol	name	Molecular structure	MW
MA	Methyl acrylate		86
MMA	Methyl methacrilate		100
EA	ethyl methacrylate		114
MAMA	dimethyl 2-methylenepentane dioate		174
s(EMA-MA)	1-ethyl 5-methyl 2-methylpent-2-enedioate		186
EMA-MA	5-ethyl 1-methyl 4,4-dimethylpent-2-enedioate		200
EMA-MMA	dimethyl 4-isopropyl-2-methylpent-2-enedioate		214

s(EMA-EMA)	diethyl 2,4-dimethylpent-2-enedioate		214
EMA-EMA	diethyl 2,4,4-trimethylpent-2-enedioate		228
MMA-MMA-MMA	trimethyl hex-1-ene-1,3,5-tricarboxylate		258
s(EA-MMA_2)	3-ethyl 1,5-dimethyl 3-methylhex-1-ene-1,3,5-tricarboxylate		286
s(EA-MMA_2)	2-ethyl 4,6-dimethyl hept-2-ene-2,4,6-tricarboxylate		286
s(MMA-EMA_2)	3,5-diethyl 1-methyl 3-methylhex-4-ene-1,3,5-tricarboxylate		300

MA-EMA2	2,4-diethyl 6-methyl 4-methylhept-2-ene-2,4,6-tricarboxylate		314

4.4.2.2 MS2A and MS2A with Tinuvin 292

MS2A is a macromolecular resin which is obtained by polymerisation of methylcyclohexanone, followed by reduction. To investigate the behaviour of the resin under artificial ageing thermal desorption/pyrolysis experiments were performed. The choice of the working temperature was based on the thermogravimetric analysis performed on the raw material.

In Figure 41 the thermogravimetric graph (continuous line) shows weight loss of the sample with increasing temperature, and the relative derivative (dashed line), obtained by heating the resin from 25 to 600°C at 5°C/min, is reported[1].

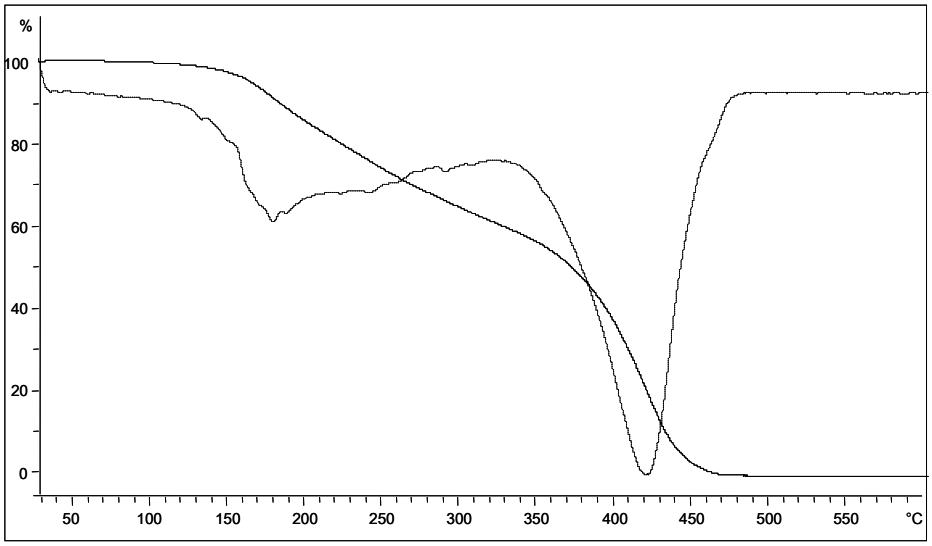


Figure 41: Thermogravimetric graph for MS2A (continuous line) and relative derivative (dashed line).

Main weight losses can be observed at two temperatures with a maximum at about 180°C and 420 °C, respectively. Based on this it was decided to submit the resin at two thermal desorption steps and one pyrolysis step, at 130 °C, 250 °C and 500 °C, respectively. The

[1] The analysis was kindly performed by Professor Valter Castelvetro, Department of Chemistry, University of Pisa.

relative chromatograms obtained by thermal desorption at 130 °C and 250 °C, and that of pyrolysis at 500 °C are reported in Figure 42.

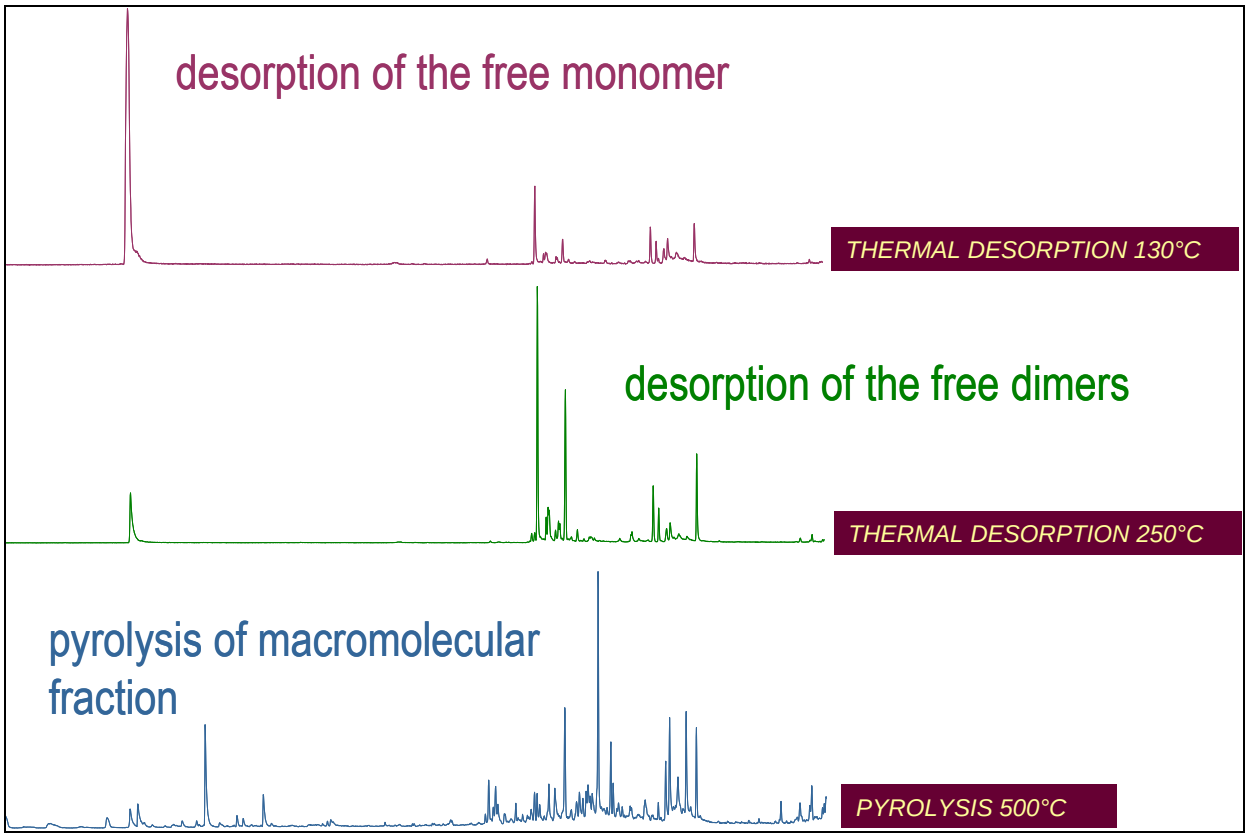


Figure 42: GC-MS chromatograms of raw MS2A exposed at 130 °C, 250 °C and 500 °C.

On the basis of the abundance of peaks on each chromatogram and from the compounds identified it can be inferred that:

- At 130°C the desorption of mainly monomers is observed.
- At 250°C the desorption of relatively low molecular weight molecules (i.e. the dimmers) occurs.
- At 500°C the pyrolysis of the macromolecular part is observed.

The analysis of the chromatograms obtained from the samples that had been exposed to artificial ageing and to exposure in museums didn't reveal the formation of any peak ascribable to oxidation products. This suggests a relatively high stability of the resin to oxidation.

The amount of the free monomers, dimers and the macromolecular fraction, depending on the diverse artificial ageing conditions, were observed to be extremely constant, both in the case of MS2A and MS2A added with Tinuvin 292. In particular:

- A possible increase of the relative amount of the dimer fraction could be interpreted as a degradation of the macromolecular fraction.

- A possible decrease of the monomer and dimer fraction with respect to the macromolecular one, could be due to the fact that these molecules escape the varnish film, constituting a potential threat for the paint films.

Figure 43 a comparison of the relative amounts of free monomers, dimers and macromolecular fraction evaluated as the sum of peak areas in chromatograms corresponding to the thermal desorption at 130 °C, at 250 °C and pyrolysis at 500 °C, respectively, is reported.

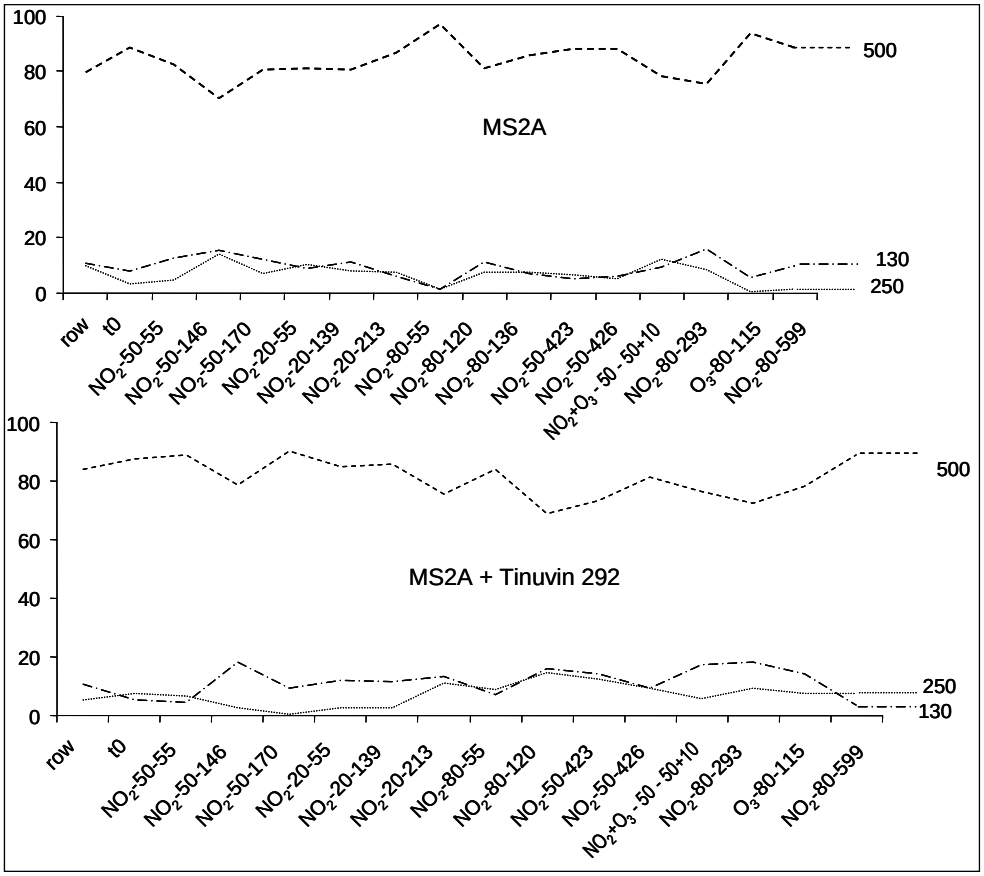


Figure 43: Comparison of the relative amounts of monomers, dimers and macromolecular fraction evaluated as the sum of peak areas in chromatograms corresponding to the thermal desorption at 130 °C, at 250 °C and pyrolysis at 500 °C, respectively.

These graphs reveal that the relative amounts of monomers, dimers and the macromolecular fraction are quite constant, indicating that no significant decomposition of the macromolecular fraction occurs under the investigated ageing conditions. Moreover, it is also possible to conclude that monomers and dimers do not escape the varnish layer.

Finally, it is extremely interesting to underline that in addition to the monomers in the chromatogram of the resins subjected to thermal desorption at 130 °C, several aromatic compounds can be seen in the chromatogram of the resin MS2A (see for the sample the chromatogram of the NO_2-80-599; Figure 44). These compounds belong to the solvent used for the preparation of the varnish samples. Aromatics were still abundant also in those samples that were exposed for a long time in the museum locations.

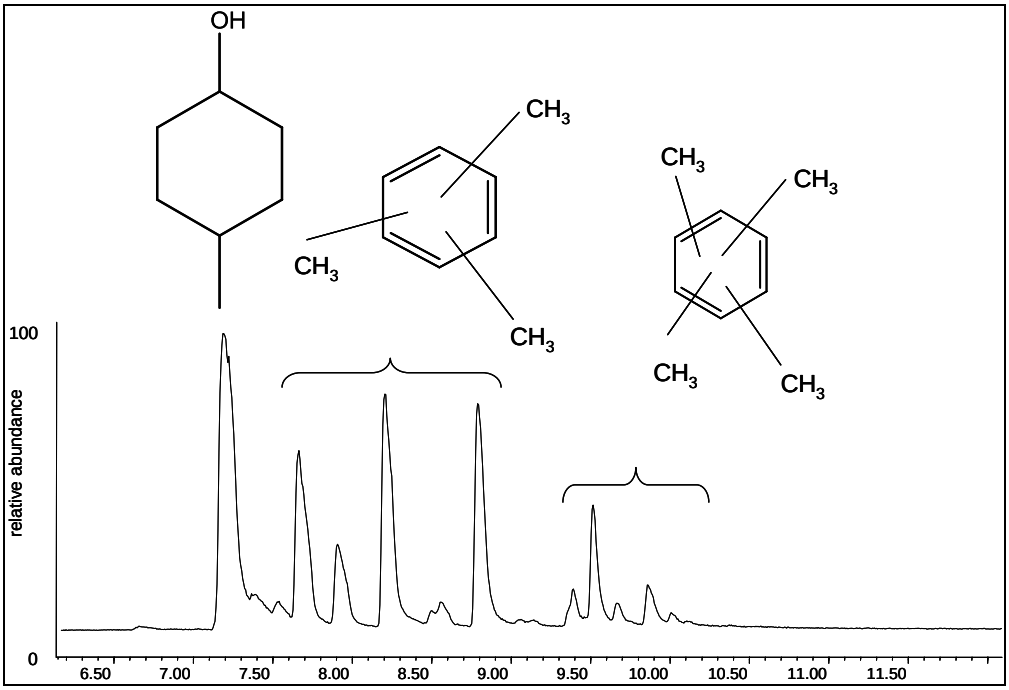


Figure 44: GC-MS chromatograms of MS2A resin of the varnish sample NO2-80-599 desorbed at 130°C.

4.5 Analytical investigations – physical aspects

The varnish samples subjected to ageing were further characterised by their physical-chemical properties, such as the softening or glass transition temperature (*Tg*). Factors which influence the value of *Tg* are: Chemical composition, moisture content of the sample, and effects of ageing which may either promote cross linking or may result in the breaking up of the structure. Glass transition (*Tg)* is the property exhibited by an amorphous polymer when it changes from a glassy to a rubbery state (or from a rubbery to a glassy state). Among the varnishes studied in PROPAINT only the synthetic varnish B72 can be considered a true polymeric material. It is a copolymer of ethyl methacylate methyl acrylate. The natural resins, mastic and dammar, contain some low molecular weight hydrocarbon polymeric components. MS2A is best described as an oligomer, containing only a few repeating units (de la Rie and Shedrinsky, 1989). Values of the softening temperature or of *Tg* can be used to understand how structural variation in the polymeric parts or the large networks can affect the visco-elastic properties of the varnishes. The Dynamic Mechanical Analysis (DMA), applied in PROPAINT, is a technique which is used to characterise the visco-elastic behaviour of materials and to determine the *Tg.*

Micro-thermal analysis was also used to determine spatial variation in *Tg* at the micron level on the varnish surface. Differential Scanning Calorimetry (DSC) using oxidative degradation was used to determine the change in thermal stability of the samples with ageing. This can provide complementary information to DMA in terms of the extent of cross linking of the samples. Results are presented for accelerated aged samples and samples exposed at sites within microclimate frames and in museum rooms. The rationale for the additional use of MALDI (Matrix Assisted Laser Desorption Ionization) mass spectrometry and SIMS (Secondary Ion Mass Spectrometry) was to determine the nature of mass fragments both in the bulk and in the surface of the samples and to support results obtained from DMA. Atomic

force microscopy (AFM) was used to provide information on the nature of the surface changes at the nanoscale level.

4.5.1 Resin Mastic

4.5.1.1 Accelerated Ageing

The softening temperatures of resin mastic films on steel were measured by DMA and compared with that of the control sample. Shifts to higher temperatures indicated the formation of a more cross linked film. Highest values and evidence of a more damaging effect were observed in resin mastic films exposed to ozone at low RH (20 %). The temperature shift was about 30^{o}C and this could be correlated with an increase in the ratio of mass fragments (523/409) in the MALDI-TOF spectra. The rationale for using this ratio was based on previous work (Scalarone, 2005) where the mass fragment at 523 was attributed to the possible formation of the oxidation product oleanic aldehyde and fragment 409 was attributed to dammardienol, the unoxidised part of the material. Figure 45 shows the effect of ozone exposure on resin mastic and the dominance of fragments in the 520 region.

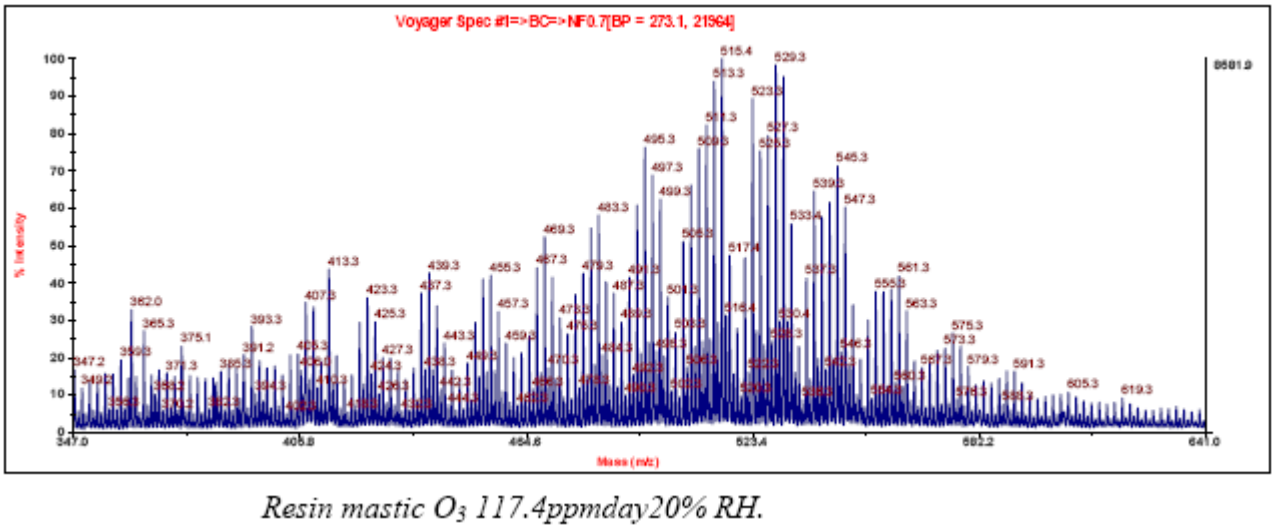


*Figure 45: MALDI-TOF spectra for resin mastic sample exposed to an O3 dose of 117.4 ppm*day at 20 % RH.*

Exposure to NO_2 also caused an increase in the softening temperature and a broadening in the measured peak at the high temperature end. This was observed to increase with dose received, and the trend was most evident for increased dose levels of NO_2 at 50%. At 80% RH the trend was not as clear. This could be due to the fact that the NO_2 possibly undergoes reaction with water vapour to form nitric and nitrous acids in the reaction:

$NO_2 + H_2O \rightarrow HNO_3 + HONO$

In addition there could be plasticizing effects of moisture on the film due to the high RH which would lead to lowering of the *Tg* .

Exposure to acetic acid also caused an increase in *Tg* and this effect increased with increase in the concentration and with RH.

4.5.1.2 Effect of damage at sites interpreted in terms of Tg of resin mastic films

The results obtained for the onset of softening of resin mastic films are discussed in terms of the environmental conditions, mainly the levels of inorganic and organic pollutant gases measured at the sites. The effect of ozone is most evident in the sample exposed in the museum in Mexico. Figure 46 shows values for *Tg* for resin mastic strips exposed in frames and in rooms. The sample in the room in the Museum in Mexico was exposed to a higher than recommended level of O_3 (19.9 μg/m^3) (Figure 47). The sample exposed inside the microclimate frame in Mexico city had the highest *Tg* value. The frame appeared not to offer any protection as the *Tg* in the frame was equally high as in the room (Figure 46 and Figure 49). Measurable levels of O_3 (1.4 μg/m^3) were present within the frame and may together with acetic acid, and light have been a contributing factor.

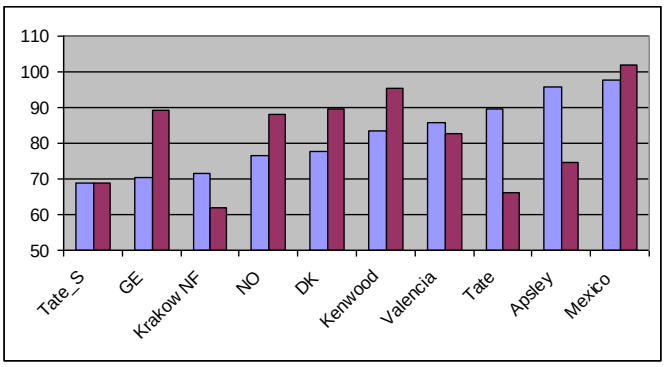


Figure 46: Tg values for resin mastic in frames (deep red) and resin mastic in rooms (blue).

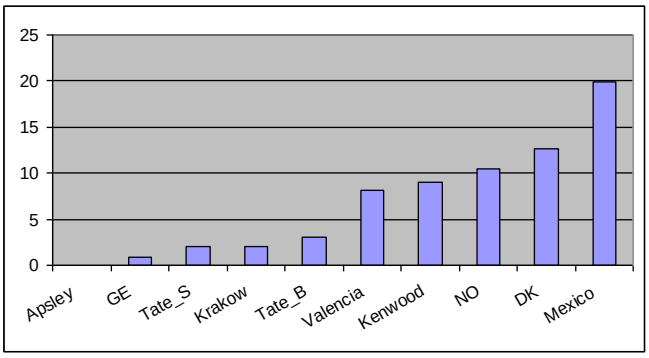


Figure 47: Ozone concentrations in rooms.

Levels of acetic acid in the Museum in Mexico were 519 μg m^{-3} and higher than those in the room (37.8 μg m^{-3}) (Figure 48), and the *Tg* was the highest of the exposed films. The frame is purpose built and similar to the one used in the Museum in Valencia, with a low air exchange value. A high *Tg* value was also obtained in the frame in the museum in Valencia, where there was a measurable level of ozone in the frame (2.7 μg m^{-3}) and an acetic acid concentration of 434.5 μg m^{-3}.

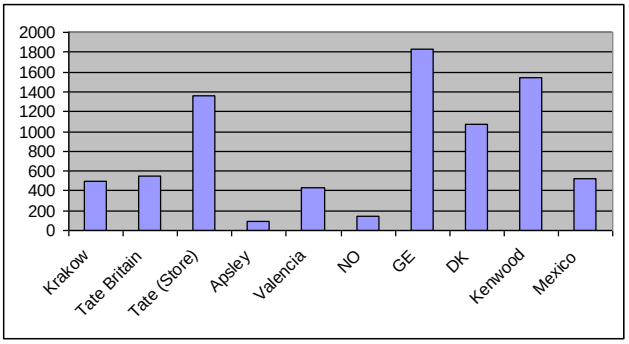


Figure 48: Acetic acid concentrations in frames.

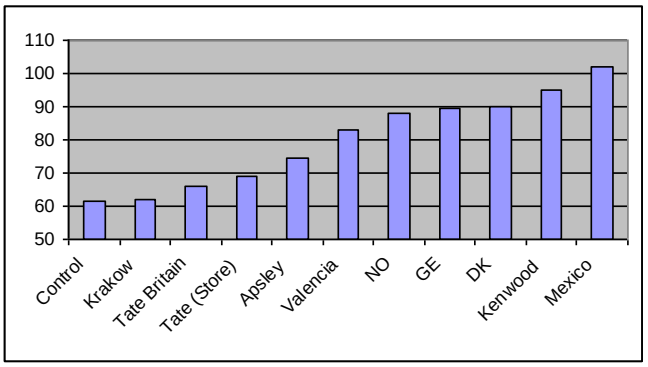


Figure 49: Tg values of resin mastic films in frames.

Samples exposed within the microclimate frames, where measured acetic acid levels were relatively high (here values are considered which are greater than 1000 µg m^{-3}), also had high values of *Tg* (Figure 48 and Figure 49).

This was the case in Kenwood (London), Statens Museum for Kunst (Copenhagen) and at the Germanic National Museum (Nurnberg). The frame at Kenwood had a high rate of air exchange and a high inner concentration of acetic acid in the frame (1547 µg m^{-3}). The frame in the museum in Copenhagen had similar levels to those measured in Kenwood and shows similar lack of protection. The newly built frame in Krakow (NMK2) offers significant protection (sample of resin mastic has a *Tg* similar to the control sample, and the frame has a low air exchange rate value). The level of acetic acid was 501 µgm^{-3}. The frame in the Germanic National Museum showed a high value of *Tg* and this correlates with the very high levels of acetic acid (1800 µg m^{-3}) in the frame.

For all the sites examined, the increase in *Tg* (Figure 50) of the varnished strips exposed in the rooms follows the increase in concentrations of O_3 and NO_2 as seen in Figure 46 and Figure 51, respectively. For the frames the *Tg* for the strips indicated some correlation with levels of acetic acid, in particular for Kenwood (London), Statens Museum for Kunst (Copenhagen) and the Germanic National Museum (Nurnberg). In the case of Tate store, though acetic acid levels in frames are high, the value of *Tg* is low and this may be also influenced by the very low light levels in the store.

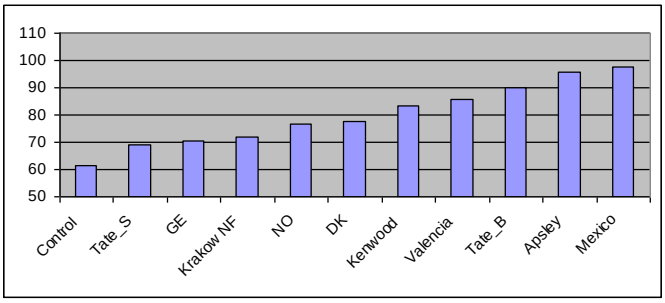


Figure 50: Tg values of RM strips in rooms.

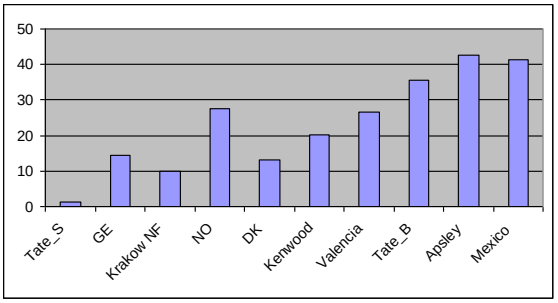


Figure 51: NO_2 concentrations of strips in rooms.

The effect of ozone on resin mastic is highest at low RH, and is lower at higher values of RH. The effect of NO_2 increases with increase in NO_2 at 50% RH. At higher humidity the effect of increasing concentrations is not as evident. *Tg* of resin mastic increases with acetic acid concentration and RH. For the sites, the *Tg* of resin mastic strips exposed in the rooms follow levels of NO_2 and to some extent O_3. For the frames the *Tg* of resin mastic strips exposed in frames show some correlation with acetic acid levels. Increase in higher molecular weight fragments (as shown by increase in ratio of mass fragments 523/409) is in accord with higher observed *Tg* values in frames for Statens Museum for Kunst and the Museum in Valencia (Figure 46). Low values for ratios and *Tg* were observed for Krakow (NMK2).

4.5.2 Dammar

4.5.2.1 Accelerated Ageing

DMA measurements of dammar strips have shown that *Tg* values increase for samples exposed to oxidising agents (NO_2, O_3) and that Tinuvin has a protective effect. It lowers the *Tg* values considerably, as it can be seen in Table 13.

Table 13: Values of Tg for accelerated aged samples of dammar and dammar and tinuvin.

Dammar DMA. Accelerated aged samples.	***Tg* Dammar**	***Tg* Dammar &Tinuvin**
DM control	71.9	59.7
DM no. 5C, NO_2(426 ppm), 50 % RH	94.7	
DM no. 7.1B, NO_2 (599 ppm), 80 % RH	96	61.6
DM, O_3, 50 % RH	84	61.6
DM, HAc, 20 % RH	82.6	
DM, HAc, 80 % RH	75.8	61.6

4.5.2.2 Exposure at sites

Tg values for dammar strips exposed at the sites are shown in Figure 52.

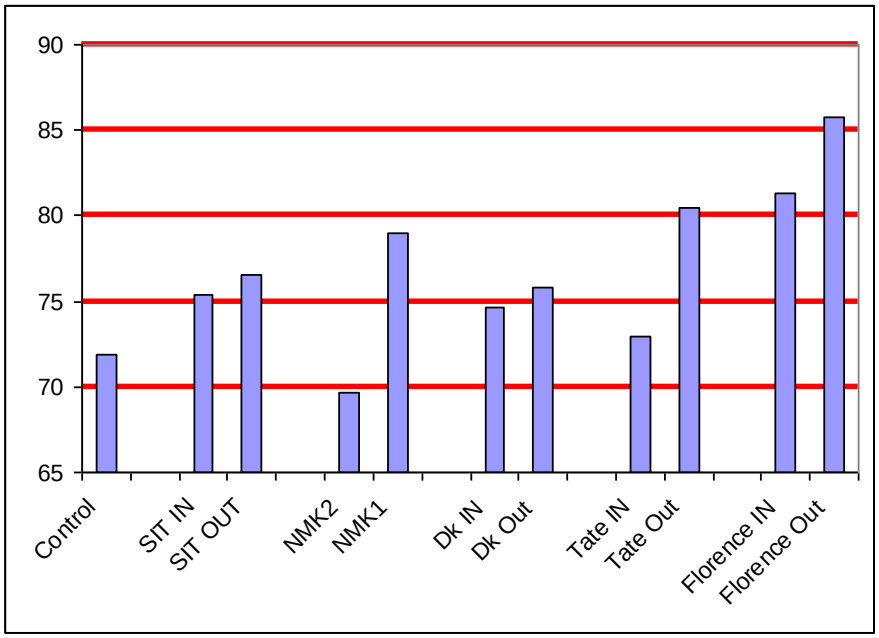


Figure 52: Graph shows the plot of Tg (^{o}C) vs. sites. IN = Inside microclimate frames. OUT = outside microclimate frames.

Dammar exposed in the National Museum in Krakow (Leonardo painting, NMK1), in the room in Tate Britain (Tate Out), and both within the showcase and in the room in the Uffizi Gallery (Florence) showed more change than in the frame and room in the Museum in Valencia (SIT IN and SIT OUT, - SIT frames were used in the Fine Arts, Valencia) and also in the Statens Museum for Kunst (Copenhagen) (Figure 52). Samples containing Tinuvin 292 in dammar and exposed for similar periods showed very small deviations from the control.

For dammar samples analysed by MALDI the ratio (497/409) was used to assess level of change (the fragment 497 corresponds to the oxidized hydroxydammarenone molecule) (Scalarone, 2005). The varnish sample exposed in the room in Tate (Tate; OUT); had a higher 497/409 ratio (3.3) than the sample exposed within the microclimate frame (1.3), which value is similar to the varnish sample control. It also has higher *Tg* (more oxidized and cross-linked) than the varnish sample within the microclimate frame (Tate; IN); the shift is about 10^{o}C. This showed that the frame is protecting the painting. A similar effect was also observed for samples exposed in the Uffizi Gallery. The sample exposed within the microclimate frame (497/409 ratio = 1.3) was less oxidised than the varnish sample exposed in the room (497/409 ratio = 4.1). The corresponding *Tg* values for the sample exposed in the Uffizi in the room was also higher; *Tg* within the frame was 82^{o}C and out of frame was 87^{o}C. Samples containing Tinuvin showed very small deviations from the control.

4.5.3 MS2A

4.5.3.1 Accelerated Ageing

The effect of oxidising agents (NO_2, O_3) and acetic acid showed some shift to higher temperatures of the softening or glass transition temperature (*Tg*). There was also a small broadening in the peak shape. The *Tg* was measured from the onset of the softening. The shifts and peak broadening effects were smaller than those observed for the natural resins. This is in line with the rationale for using MS2A for its improved stability compared to natural resins (de la Rie and Shedrinsky, 1989). Some variation in the shape of the peak for the control sample was observed and could be attributed to the presence of varying levels of trapped solvent reported in the GC/MS part of the work. This would have the effect of lowering the Tg due to plasticization effects.

4.5.3.2 Exposure at sites

Values for the sites tested showed overall small differences. For the strips exposed in the museum in Valencia a lower value for *Tg* was measured in the frames and this could be due to plasticization effects due to trapped solvent and the low air exchange rate of the frame. In the sample exposed in the room in the Statens Museum for Kunst (SMK1) the value of Tg was higher than in the microclimate frame sample, and this could be attributed to the action of oxidising agents on the film, as higher *Tg* values were also observed for the NO_2 exposed sample. The higher value was also accompanied by observations that the film was more brittle than inside the frame. DSC studies confirmed that values for SMK1 were higher than for Valencia, indicating that some cross linking had occurred.

4.5.4 Paraloid B72

4.5.4.1 Accelerated Ageing

Samples of Paraloid B72 were found to be most damaged by ozone. Images obtained by Atomic Force Microscopy (AFM) revealed significant changes in the surface and formation of pits. Figure 53 shows the effect on the surface of exposure to ozone at 80% RH. The damage to the film was also found to affect the shape of the DMA curves. Surface characterisation using SIMS showed the nature of the chemical damage that had occurred. Indications are that there is depletion in the surface of ethyl metacrylate by the oxygen radical O• and this appears to occur to a greater extent in the "dry" (i.e. 20% RH) environment. In DMA small shifts in the *Tg* were observed to higher temperature together with changes in peak shape. Exposure to acetic acid at 80% RH also had an effect on the films.

4.5.4.2 Exposure at sites

Changes were observed in strips exposed in the National Museum in Krakow. As for MS2A the changes in terms of shift in *Tg* were less than for the natural resins, and also for the exposure at the museum sites less than for the accelerated aged samples. For samples exposed in location NMK2 (Cracow new frame) the changes as measured by DSC were small and those for the location NMK1 were greater, and in the direction of damage induced by oxidising agents. This was supported by SIMS data. The NMK2 exposed sample had similar SIMS fragments to those of the control while the one exposed in NMK1 showed a depletion of both ethyl metacrylate ($C_4H_5O^+$) and methyl acrylate ($C_2H_3O^{2+}$). The NMK1 frame has a high air exchange rate and so offers little protection to the varnish of the painting.

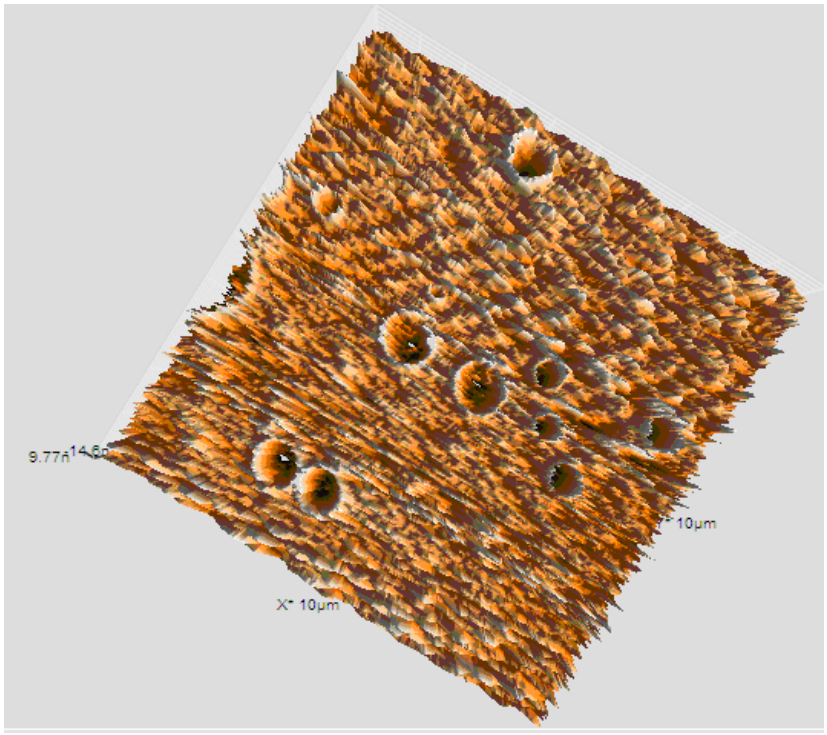


Figure 53: AFM image (10 µm x 10 µm) of B72 exposed to NO_2 (4ppm for 27 days) at 80 % RH.

5 The functioning and protective properties of microclimate frames for paintings

5.1 Summary

During the PROPAINT project, improved knowledge about the required design and performance of microclimate frames has been obtained. This will contribute to a higher standard within preventive conservation of paintings in display, transit or storage. The most important properties of microclimate frames and standards for micro environments for paintings have been investigated and defined. Acceptable environmental levels, design issues and monitoring possibilities have been key topics of the work that have been carried out in laboratory tests and by testing of existing and new-built frames in different end-user locations. Furthermore, state-of-the-art knowledge about microclimate frames has been collected from the literature as well as from small and medium enterprises (SMEs) and institutions working with microclimate frames.

A mathematical model for calculating the interdependent properties of microclimate frames has been developed. This kind of modelling provides a tool for evaluating the performance of existing frames, and for designing new frames. Also, as part of the PROPAINT project, a Decision Making Model for the design of microclimate frames has been created.

The results achieved in the PROPAINT project have furthermore resulted in a number of comments and suggestions for a new standard on showcases, presently in public enquiry, from the European Standardisation Organisation (CEN).

5.2 Implications for preventive conservation

In order to evaluate existing microclimate frames and improve the future designs it is necessary to define the qualities of efficient microclimate frames and the means to construct efficient microclimate frames. The PROPAINT project has collected detailed information from existing experiences and evaluated the properties of microclimate frames qualitatively. This information is an important part of the results achieved in PROPAINT and may be implemented in conservators practical work with microclimate frames and in future projects related to the design and use of microclimate frames as a preventive conservation strategy.

From the mathematical modelling, it has been possible to show the correlation between the air exchange rates of microclimate frames, their geometric properties (volume and internal area) and their levels of internal pollutants. When applied to different existing microclimate frames the modelling showed that most of the frames do protect the paintings against impact of gaseous pollutants. This evaluation does however depend on comparison and “weighing” of degradation impacts mostly from inorganic and oxidizing, gases that infiltrates from outside. In addition organic and acidic gases, mostly emitted inside the microclimate frames, have to be taken into consideration. However, due to high internal emissions of organic acids the frames do not fulfil the general recommended criteria (or standards) for acceptable levels of exposure to the pollutant gases. For some microclimate frames the total load of pollutant gases to the painting will be reduced by tightening the microclimate frame as much as possible, to hinder infiltration of pollutants from outside of the frames. For other microclimate frames the total load of pollutant gases will be reduced by increased out ventilation of pollutants that off-gas from the painting and the frame itself. However, due to the small volumes of most microclimate frames and the common large emission and deposition fluxes

of the internally emitted organic pollutant gases inside the frames, as compared to the amount of pollutant ventilated out for every air exchange, the effect of a moderate or even quite high increase (e.g. from d^{-1} to h^{-1}) in ventilation is usually slight. Thus, other mitigation measures such as installation of barrier films and/or absorbing media inside microclimate frames are usually recommended to lower the potentially degrading impact of gaseous pollutants on the paintings. The information from the mathematical modelling can enable decisions on alterations of the frames in order to optimize the internal environment. The modelling showed that, although the working principles for microclimate frames are similar, each case should be treated separately and decisions to be made individually for the design adjusted to each painting.

Based on the debate of issues introduced by the PROPAINT project and the research results from the project a model for decision making for construction of microclimate frames has been developed. The model does not contain ultimate instructions for the design of microclimate frames, but is intended to be a practical helpful tool which, combined with the state-of-the-art research results, may assist further development of microclimate frames by producers and for museum professionals. This should facilitate and improve the design of microclimate frames and thus benefit the state of preventive conservation for paintings enclosed in microclimate frames.

The project has provided new knowledge to commercial manufacturers of microclimate frames and museum professionals, – enabling them to adjust their designs towards better and more flexible solutions. Thus, the PROPAINT research has had direct influence in improving the quality and properties of microclimate frames available for museums and collections. The preventive conservation of paintings has thus been facilitated, as more information is available to provide the best possible quality of the microenvironments for each painting at its specific location.

Some problems and issues related to the use of microclimate frames have been brought to attention during the PROPAINT project. The possible accumulation of internally generated emission products inside the frames is one important issue. Another issue is the so-called *ghost images*[2]. Research on both topics has provided new information that can help in finding solutions to these problems for preventive conservation.

The continuing research about microclimate frames can improve the existing means of preventive protection. Preventive conservation, such as enclosure of paintings in microclimate frames, minimizes potential risk of damage and degradation and therefore the need for active, intervening conservation treatment.

The research performed during the PROPAINT project has resulted in several comments on the relevant CEN-standard proposal[3]. As such, the research within the PROPAINT project may have direct implications for future standards. The research on microclimate frames within this project has also contributed a lot to the knowledge that forms the basis for future work on this topic.

[2] See Appendix 4 for a case study in the Mauritshuis museum (The Hague, Netherlands), performed with the PROPAINT project, about the formation of ghost images on the glass in microclimate boxes.
[3] See Chapter 6.7: Standards for microclimate frames for paintings

5.3 Decision Making Model for the design of microclimate frames

A major aim in PROPAINT has been to suggest the most suitable design and construction features for microclimate frames, for optimizing the preventive conservation of paintings. In order to facilitate the design of future microclimate frames, a model for decision making was developed. The model is based on findings from various analyses of data from the PROPAINT research, as well as on current state-of-the-art knowledge derived from the conservation literature.

The main focus in the general discussions about microclimate frames in the literature has, until recently, been on the establishment of an environment with a stabile relative humidity. The literature describes the use of active buffer materials or the paintings' own buffering capacity in well sealed enclosures (Hackney, 2007; Richards, 2007) to stabilize the internal relative humidity in microclimate frames. In addition, more recent literature reflect an increasing interest in pollution levels inside microclimate frames and in problems related to emission from internal frame materials. In relation to these topics, control of the air exchange rate (sealing of frames) and modified atmospheres have been discussed (Shashoua, 1999; Thickett et al, 2007; Ryhl-Svendsen et al, 2009).

PROPAINT investigated, in particular, the air quality inside microclimate frames as affected by external as well as internal factors. A large measurement campaign (Chapter 4) was carried out, and air quality and climate measurements were performed inside and outside microclimate frames for paintings in European museums and overseas (Table 3), as well as at a frame producing company. The results were essential for the understanding of the importance of several frame design parameters, e.g. the influence of the air exchange rate on pollution concentration and fluxes.

State-of-the-art knowledge about important properties of microclimate frames has been collected and four examples of state-of-the-art microclimate frame models are presented in this report (Figure 58 – 61, 2D drawings). The decision making model is shown in Figure 53 and includes knowledge obtained from experiences of the two frame-builder workshops; National Museum in Krakow and SIT, Madrid in their work to develop and refine microclimate frame design based on the PROPAINT research. A general conclusion based on experience from frame building is, that the concept of "microclimate frame technology" is not a serial manufacturing process. The building of microclimate frames depends on individual properties of the actual painting that is to be framed.

The most important property of microclimate frames is that they are barriers against fluctuations of the outside conditions during exhibition, storage, and transport. They stabilize the microclimate around the painting; they protect from dangerous mechanical damages, including vandalism, during exhibition or travel, and they reduce levels of gaseous and particulate air pollution. In general, microclimate frames provide a low-risk environment when they are built from carefully selected materials. The main finding that can be singled out is an advice to keep microclimate frames as air tight as possible, if at the same time the interior pollution level can be kept low by the use of non-emissive materials and the object itself is low-emitting, or by the use of pollution scavengers.

The PROPAINT Decision Making Model

The PROPAINT Decision Making Model (Figure 54) seeks to suggest a work plan including five steps that one should consider before and during the designing process of a microclimate

frame. It is not possible – or even advisable - to suggest one ultimate frame design or to create a "check list" for microclimate frame designing.

However based on the research performed, the PROPAINT Decision Making Model includes the following five steps:

- Investigation of present and future conditions and restrictions, and assessment of risk factors;
- Definition of target for action;
- Definition and choice of design alternatives;
- Implementation of decisions;
- Evaluation of decisions.

Furthermore, references to research results will be given, which may be beneficial to consult for relevant information. The aim has been to create a practical tool for designing, selecting or evaluating microclimate frames in order to provide the best possible preventive conservation setting for each individual painting.

As a starting point of the design process, there are a number of central issues to be investigated and defined. Knowing the present composition and condition of the painting and the ambient environment that it is subjected to is essential. Therefore the proportions, material composition and condition of the painting must be investigated. The future location of the painting and microclimate frame must be known: Is the frame intended for permanent exhibition, for storage or for travel and how are the environmental conditions at the location of display, storage or transit? Climate levels, pollution levels, light exposure levels and the possible danger of mechanical damage should be investigated through a risk assessment. Furthermore, one must know the relevant restrictions (economical, aesthetical, legal, etc.). These issues must be held in mind during the entire design process.

Knowing the composition and preservation condition of the painting, the next step is to define the acceptable environmental levels for climate, pollutants, and light/UV radiation inside the microclimate frame. This should be done using the most recent knowledge on the subject. Comparing the present or assessed future condition, the target levels can indicate which properties and functions the microclimate frame must possess.

The design of a microclimate frame implies choice of construction method and materials and these factors will determine the properties, functions, cost and aesthetics, etc. of the microclimate frame. Investigations into different design alternatives could be based on questions such as:

Construction:

- How can the acceptable climate levels be achieved by means of construction?
- How can the infiltration of ambient pollutants that may harm the painting be reduced?
- How can ambient pollution and pollution generated internally in the microclimate frame be dealt with?
- How can the painting be protected from mechanical damage or vandalism?
- Should the microclimate frame be environmentally monitored – and how?
- Shall the existing, historical frame be used or shall a new frame be constructed?

Materials:

- How can emission of harmful pollutants from materials inside the frame be avoided?
- Which materials give the best protection against harmful light/UV radiation exposure?
- How can aesthetical demands be met?
- How can a long life time of the frame be secured?

These are only some of the questions that arise in the process of making the necessary decisions before actually constructing the microclimate frame. Answers must be found in the literature reporting the most recent research results on the different topics. The questions must be weighed against one another and prioritized, as choices can affect each other. For example, a very well sealed microclimate frame can provide a very stable humidity level but at the same time increase the level of pollutants emitted from materials inside the frame, – if this problem cannot be solved by the choice of construction materials or by other means.

All choices must be made using the most recent knowledge about control of environmental conditions in microclimate frames. Analysis of data from the measurements performed as part of the PROPAINT research has provided new information. Experience and evaluation of existing frames, literature studies as well as mathematical modelling furthermore support informed decision making.

Once the microclimate frames have been constructed and are used, evaluation of the design can be carried out by monitoring of the condition inside the microclimate frame over time. This can be done by using climate data loggers and pollution dosimeters enclosed in the microclimate frames and by comparing the measurements to the previously defined, wanted environmental levels or to newer standards defined in recent literature. In previous EC projects (MASTER EVK4- CT-2002- 00093, MIMIC EVK4 -CT-2000-00040 and AMECP, EV5V-CT-92-0144) “standard levels” were suggested and monitoring technology have been developed in order to facilitate the investigation and evaluation of environmental conditions for objects of art.

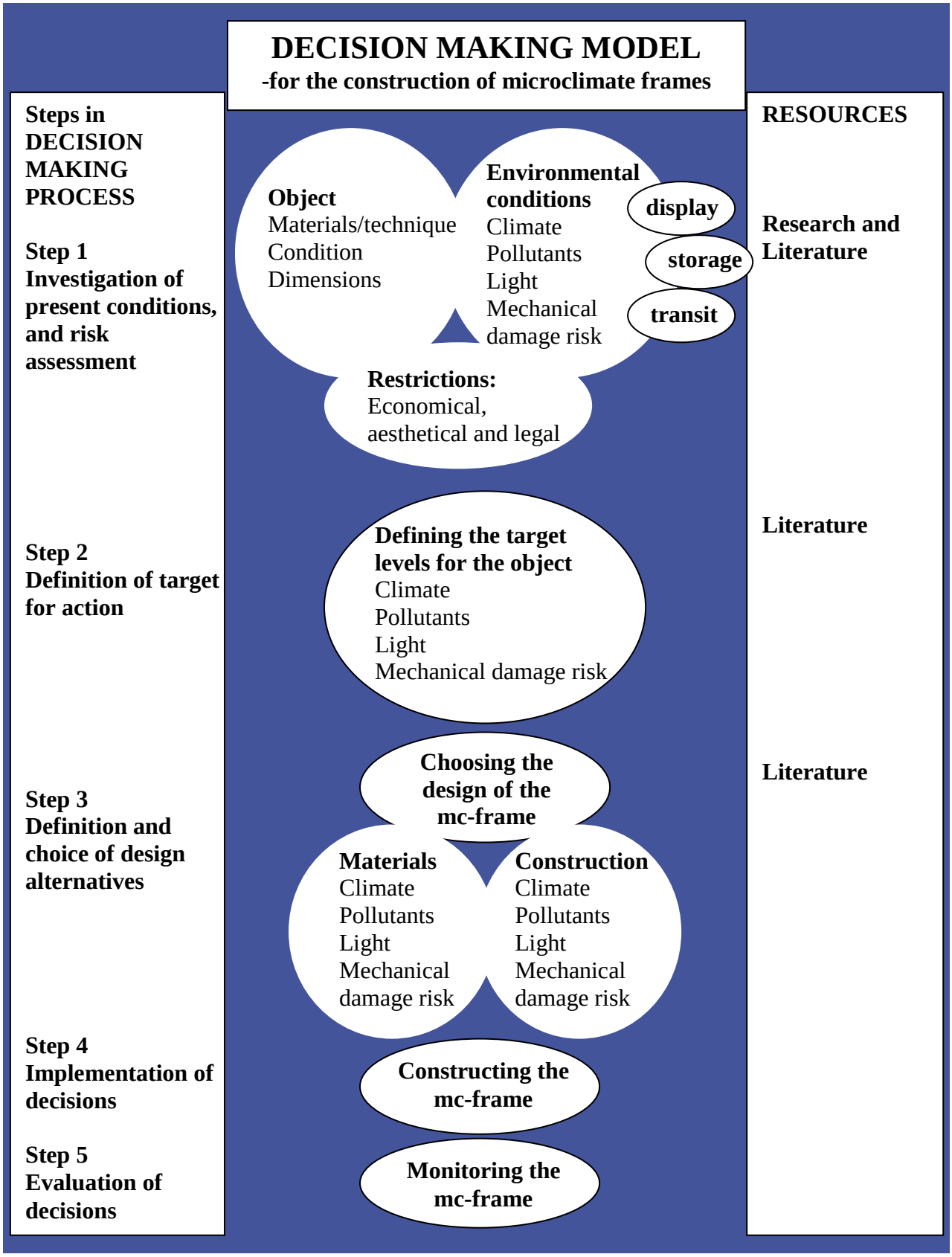


Figure 54: The PROPAINT Decision Making Model (mc-frame: microclimate frame).

5.4 Important properties of microclimate frames

As a result from the work of producing and using microclimate frames, some of the PROPAINT partners have discussed their experiences about the essential properties of microclimate frames. Some important properties of microclimate frames generally agreed upon are presented below.

Individual design
Microclimate frames are individually built for every individual painting to be enclosed. Paintings are complex structures with characteristics depending on each painting's technique, age, preservation state and dimensions. Furthermore, the required performance of a microclimate frame depends on the environmental conditions of the present and temporary, or future locations of the painting. Therefore, designing microclimate frames cannot be done as a serial manufacturing process.

Materials
The materials used for the construction of microclimate frames should be of high quality and be stable over the long term. Care should be taken to avoid emission of harmful gasses, such as organic acids, inside the microclimate frame by using inert materials, avoiding emissive finishing coatings and by sealing off any emissive surfaces.

Air exchange rate
The air tightness of a microclimate frame defines the level of efficiency to protect the painting against ambient pollutants and environmental variations. If the artworks are kept in a totally climate controlled and clean air room, the sealing capacity could be lowered. However, the reason to enclose the artwork in a microclimate frame is often to protect the fragile structure during travel, temporary loan periods, moving or even periods of storage. In most of these situations the environment is less stable or controlled, which is often the major reason for the use of microclimatic systems and frames. Even enclosures that are not very airtight reduce the air flow significantly and thereby improve the stability of climatic conditions inside the frame. Nevertheless it must be taken into consideration that frames with high emission of organic acids can act as green houses to the paintings preserved inside. In these cases sealing off any emissive surfaces of the frames could be an efficient solution. When this is not possible and the concentration of inorganic pollutants in the room is reasonable low, a higher air exchange ratio might be advisable.

Humidity buffering
The use of humidity buffering materials in microclimate frames is an ongoing topic of discussion. If buffer materials are included in microclimate frames, the type and amount of buffer material should be carefully chosen and calibrated in relation to the properties of the enclosed painting and the air volume inside the microclimate frame.

Often, the buffering capacity of the painting itself is sufficient to maintain a stable humidity level inside a microclimate frame. In this case, factors such as low air exchange rates and suitable mass of object to volume of microclimate frame ratios play an important role.

Scavengers and sorbents
The use of materials for neutralization of pollutants in the microclimate frames is a topic of discussion. Materials such as active coal or oxygen scavengers can be included in a

microclimate frame if needed. However, the efficiency and lifetime of such products must be investigated further.

Monitoring, control and follow-up
The performance of microclimate frames can be measured by dosimeters. Continuous monitoring by means of an internal data logger is possible for some types of dosimeters. A simplified evaluation graph which shows the information obtained from measurements is needed. Evaluation charts are useful tools for the people responsible for the artworks, to make decisions and protect their cultural property.

Visual inspection of both front and back of paintings mounted in microclimate frames can be important and can, at least to some degree, be possible by using transparent backing such as polycarbonate sheets.

Long term efficiency
The lifetime of microclimate frames depends on the materials and design used in the construction of the frames. Furthermore, long term efficiency can be improved by the use of some simple means:

- The design of a microclimate frame should assure an efficient and simple mounting process. This means that no complex tools should be used during the installation. All the mounting should be possible with simple and small tools and the complete process should be performed under clean conditions and be efficient and reasonably expedite. All materials used, - as well as the painting, should be conditioned to the same temperature and relative humidity prior to the mounting.

- It is advisable to prepare and include the hanging or support system as part of the total frame system. Because of the sensitive structure and seal of microclimate frames, any additional drilling or fixing on the back of the frame should be avoided in order to preserve its efficiency.

The characteristics of each different microclimate frame should be identified with a technical label placed clearly visible on the back cover. The label should be in place whether the painting is intended for loan or not. The label should inform that the frame is a microclimate frame that should not be opened. Furthermore, the label could contain information such as:

- Inside dimensions and air volume;
- Estimated surface area and volume of solid material inside;
- Recommended levels of RH and T inside the frame;
- Material and technique of the art work;
- Notes and comments from monitoring programmes;
- Date of sealing;
- Conditions (RH & T) in the place where the microclimate frame was sealed;
- Date and conditions (RH & T) in case the microclimate frame has been opened;
- Name/signature/date of the installer and of the person responsible for the artwork.

Aesthetics
The choice of glass is an important factor when it comes to the aesthetical outcome of microclimate framing. The glass should be non-reflective, fully transparent and colourless.

Whether or not the original frame is reused in the construction of the microclimate frame, the visual appearance of the frame itself should be carefully considered.

Economy
The expenses of building and maintaining microclimate frames are, naturally, an issue in most situations. At the National Museum in Krakow the building of frames is carried out by their technical personal in cooperation with the museum's conservators and the price is described as relatively low. Furthermore, they stress the point, that microclimate frames reduce the need for climate control on room level.

Handling safety
The size and weight of a microclimate frame should be considered in relation to its handling. With the development of microclimate frame designs, in its different variations, and the improvement of building materials the general dimensions (weight and size) of microclimate frames are constantly reduced. New technology glass, aluminium, non woven fabrics, polycarbonate panels etc. help to optimize the design and performance.

Microclimate frames protect the enclosed paintings against mechanical damages, - both risks related with handling and transportation and risks of vandalism or accidents in display locations.

5.5 The building process and designs of microclimate frames

5.5.1 End-User Survey

One task in the PROPAINT project was to investigate the current microclimate frames found in museums in order to quantify and describe the different types of microclimate frames currently in use. This was investigated within the group of end-user museums of the PROPAINT project by distributing a two-step questionnaire about:

- Characteristics of microclimate frames and ambient sites;
- Framed artworks; their condition and conservation history.

The questionnaires revealed several similarities in the designs of various microclimate frames, as well as a few distinctive differences. The following provides an overview, whereas detailed information is found in Tables 3.1 - 3.6 in Appendix 3.

- Most frames were built within an existing frame (a modified historical frame) and most frames have recently been modified into microclimate frames.
- Most of the microclimate frames are movable in size, except the Leonardo frame in the National Museum in Krakow, which is a build-in showcase.
- The frame volumes ranged between 0.011 m^3 and 0.084 m^3. The inner surface areas ranged between 0.468 m^2 and 2.90 m^2. The Leonardo frame is larger with a frame volume of 0.315 m^3 and an inner surface area of 5.07 m^2.

The inner dimensions of the various frames are reported in Table 3.2. The dimensions of the enclosed paintings are listed in Table 3.3. Total area of the frames, the frame net volume, and painting/frame inner area ratio are given in Table 3.4 (all tables in Appendix 3)

5.5.2 Construction materials

A range of different materials has been used to build the frames. The most common materials are the cover glass, which is held in place by a strainer of wood from the original frame, or by a purpose build strainer of metacrilic (plexi) or aluminium profiles. Aluminium tape or sheets are most often used to seal the wooden strainers, but polyethylene (PE) film has also been used. The backing is commonly polycarbonate sheets, but a few frames have aluminium sheets and oil tempered hardboards. The materials are held together by aluminium tape, brass and/or steel screws.

Only the SIT frames and the frames from English Heritage have humidity buffer material enclosed in the frame (Art-Sorb).

5.5.3 End-User locations

All but three of the microclimate frames (Table 3) were part of permanent exhibitions at the test sites and exhibited in public galleries or in a staircase between gallery rooms. The remaining three microclimate frames were located in a storage room (Tate Store), in a workshop area (SIT) or used for art transport during the test period (SMK2).

The exhibition rooms in most cases have plaster walls with acrylic emulsion paint. The floors are made from lacquered wood, vinyl or cork. The rooms often have several windows or a ceiling of windows. In most cases, precaution has been taken to reduce exposure of UV radiation by using filters or blinds. The lighting of the rooms and paintings is often a mixture of natural daylight, fluorescent light and halogen spots. In a few cases UV filter on the lightings is used (Table 3.1, Appendix 3). Most exhibition rooms have natural ventilation with winter heating, but no air conditioning (Table 3.5, Appendix 3).

5.5.4 Examples from producers of microclimate frames

A presentation about the experiences from the construction of microclimate frames is made by a professional company producing the actual frames and by a museum producing and using the microclimate frames.

5.5.4.1 Experience by the SME Company SIT International Transporters, Madrid

Microclimate frames mainly aim to control lighting, humidity and temperature. These are key issues in preventive conservation when keeping works of art in a sealed case, so that the surrounding environmental conditions are considerably buffered and stable.

Sudden changes seldom happen in the artworks' normal environment, except under certain circumstances (as when paintings are in transit), but seasonal changes may cause temperature fluctuation and then affect the relative humidity parameters. These variations are prevented and minimized by the components of a microclimate frame.

Each microclimate frame system is designed and built for a unique artwork and only suitable for the individual artwork which it is intended for. According to our experience, a standard general design adaptable to all kinds of paintings could potentially be harmful to the protection and stability of the object inside the microclimate frame.

Materials

A primary requirement for SIT, when building microclimate frames, is to include a buffer inside the frame, usually behind the artwork in order to minimize humidity changes. The buffer material must be a high quality stabilizer material such as silica gel precisely calibrated in relation to the air volume inside the frame. This material inside the microclimate frame provides stability in case of unexpected changes in the ambient environmental conditions.

New buffers to neutralize pollutants are used in specific situations, mainly to prevent harmful reactions caused by internal emission of gasses from the microclimate frame building materials, from the artwork itself or from recently applied conservation/restoration materials. Careful analysis should be considered when choosing the type and amount of this new generation of buffers.

A microclimate frame is manufactured in quality materials following the specific design and size of the painting. The outer surface of the materials is usually plain to ensure good adhesion of the finishing layer(s) (frequently "old appearance" gilding or acrylic colour) which is only applied on the outside. For conservation reasons it is advisable to maintain the inner side without finishing and as clean and inert as possible (Figure 58).

The lighting levels are usually regulated from an external point (as part of the exhibition gallery lighting system), which keeps the recommended light intensity regarding the fragility of the exhibited material. However, the microclimate frames incorporate an antireflective and laminated safety glass that is 2 - 4 mm thick, depending on the dimensions of the microclimate frame. The glass is fixed inside the microclimate frame or inside the original frame depending on the design.

The mounting materials selected to use inside the microclimate frame must guarantee the highest quality and conservation standard. They must be:

- Acid free;
- Long term stable
- Reversible

Design

The design of a microclimate frame is a unique work only suitable for the individual artwork which it is intended for. According to the experience of SIT, a standard general design would not be suitable to all kinds of paintings. It is irrelevant whether the microclimate frame is external, visible or hidden. The characteristics of the artwork determine the design. Elements that always should be required and considered are:

- Conservation reports on the object.
    - Material deformities (stretcher, support, frame …).
    - Fragility of the structure and finishing.
    - Missing or removable parts.
    - Biological attacks.
    - Recent conservation treatments.

- Museographic requirements.
    - Colour, finishing, supports, hangers…

SITs conclusion on the concept of microclimate frames technology is that they are not intended for a serial manufacture process. The design of a microclimate frame begins with a first technical approach to the artwork of concern studying the dimensions of the object. With the dimensions, drawings and pictures of the artwork it is possible to define the "design" of the microclimate frame in the workshop; then, the internal and external height, width and depth of the case and the exact dimensions of each part to be produced could be established.

Environment

Most of SITs microclimate frames have a mini climate-data logger installed inside to register temperature and relative humidity. The data should be unloaded periodically (first after 30 days, then after 90 days and, finally, after a year). This monitoring will enable to verify the quality of the environmental conditions and, if necessary, make corrections to the frame in appropriate time.

Records taken through years have demonstrated that environmental conditions inside the microclimate frames are quite stable, in particular during transit, when parameters inside microclimate frames are more adequate than those registered in standard transport cases and highly superior to the conditions in other different means of transport. Figure 55 - Figure 57 show recorded climate inside three microclimate frames provided to customers by SIT:

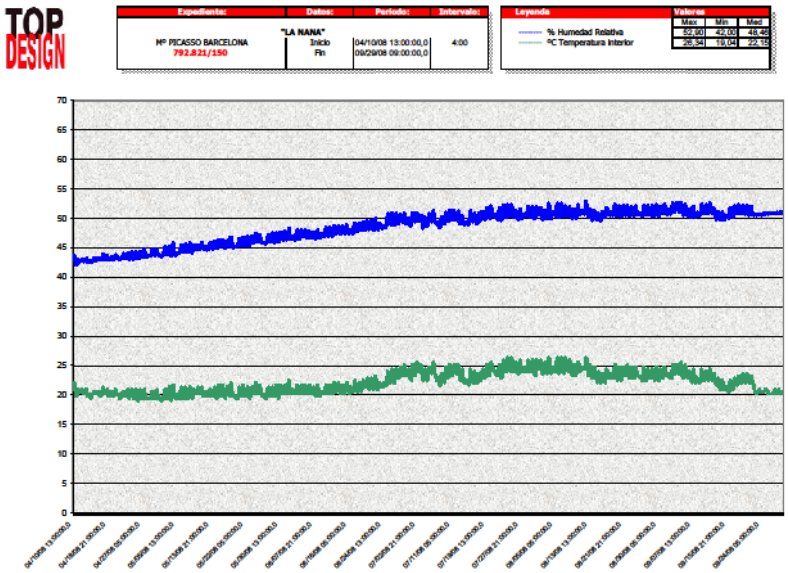


Figure 55: Temperature and relative humidity recorded inside the microclimate frame for the painting "La Nana" In the Picasso Museum, Barcelona, Spain.

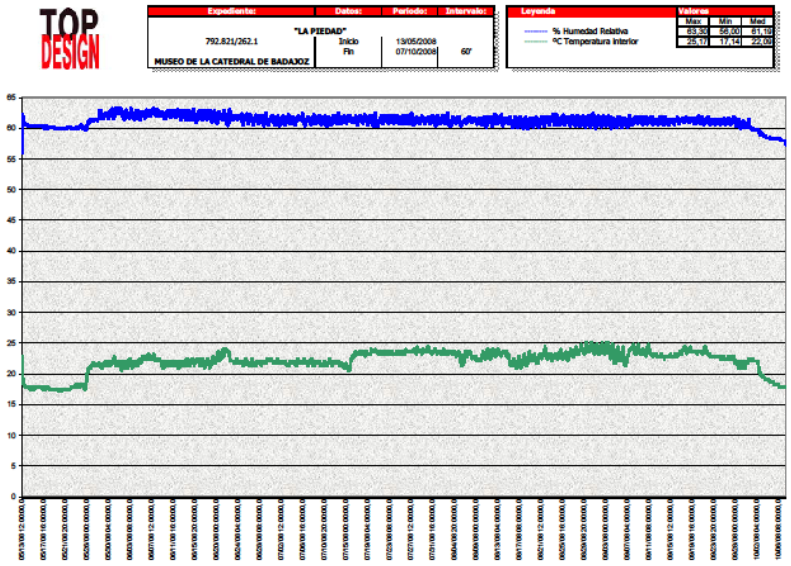


Figure 56: Temperature and relative humidity recorded inside the microclimate frame for the painting "La Piedad", Museum of the Cathedral in Badajoz, Spain.

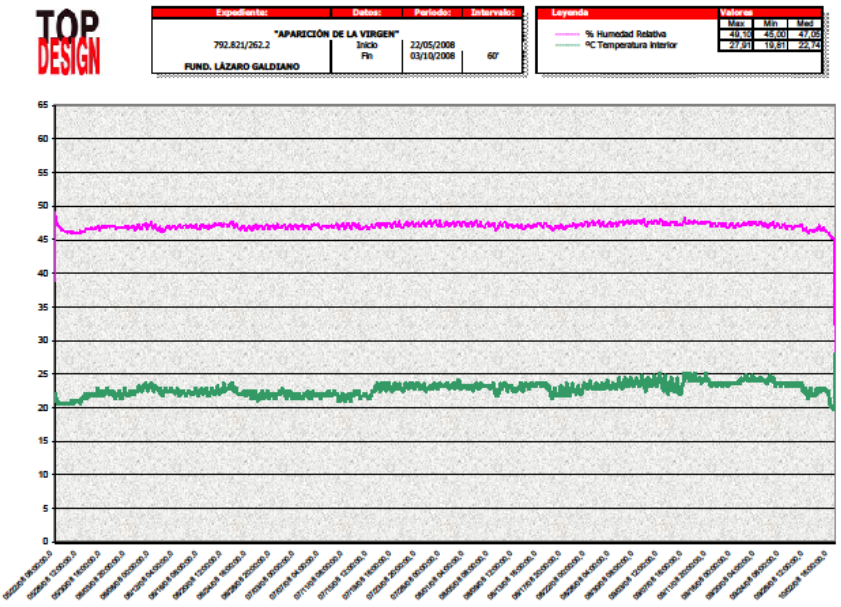


Figure 57: Temperature and relative humidity recorded inside the microclimate frame for the painting "Aparición de la Virgen" in Fund, Lazaro Galdiano, Madrid, Spain.

Recent technologies offer the possibility for simulation of the expected environmental conditions in exhibition galleries, in storage, inside cases or in any other display equipment, as well as in packing systems for transportation. With this simulation tool it is possible to analyse how the environmental conditions behave inside a microclimate frame prior to the building of the microclimate system. This study involves a detailed analysis of every component and material. The different microclimate frame elements have been drawn in the simulation programme using AutoCad©. According to the materials, manufacture process and assembly systems, the simulation programme shows the stability of the inside environment and the way to improve the environmental conditions with micro ventilation and filter equipment which would improve the microclimate frame performance.

Recent restoration treatments

Many artworks undergo conservation/restoration treatments before going into temporary exhibitions and the enclosure in a microclimate frame is often considered as a means of protection. All the materials or substances used in conservation treatments should be totally dry and cured before the painting is mounted in a microclimate frame. SIT International Transporters recommend a period of at least three months between finishing the treatments and enclosing the painting in the microclimate frame, but the waiting period should be as long as possible to obtain an internal atmosphere as neutral as possible.

Improving conservation

The long experience that SIT has with use of modern microclimate frames (more than 500 units since the early 1990's) has made it clear that the preservation state of art works is improved when they are situated in a good and stable environment with constant climate parameters. Now, with the knowledge obtained during the PROPAINT project, it is also possible to provide a cleaner atmosphere in which the objects are better protected from pollution, changing environments and even from vibration during transit.

Improvements based on PROPAINT research

The experience and results obtained from the PROPAINT project have identified for us some elements in the design, manufacture and assembly of the microclimate frames that have already been modified and improved.

The air exchange tests have shown low values of air exchange rate (AER) as an important parameter. PROPAINT tests have confirmed that the microclimate frames from SIT have got this feature and air exchange rates are now specified and measured for all frames. When museums entrust their paintings for lending periods, storage and transit, they expect that those paintings will be "isolated" from any changing environment (uncontrolled, extreme or polluted) outside the museum controls. Therefore, the goal was to achieve the highest level of air tightness for the long period of time.

In more than five hundred units which have been designed, manufactured and assembled by SIT, neither damage nor alteration on the artworks has been detected because of the airtight seal inside the microclimate frame. On the other hand, unstable paintings exposed to severe environmental changes (in relative humidity and temperature) experienced constant alterations before being protected by the microclimate frames. This was the case for several paintings on panel, but their structural stability showed an outstanding improvement as soon as they were isolated and stabilized by means of calibrated silica gel inside the microclimate frame. These experiences go back to the early 1990's, so their historical interpretation could be quite short comparing with the time the works of art have stayed among us. However, the

information that the PROPAINT research has provided makes us aware of the relevance of knowing, assessing and, if necessary, improving the air quality inside the microclimate frames, since this air is in direct contact with the protected painting.

To summarize, our present research on microclimate frames is focused on obtaining the best air quality possible combined with the option to choose between an airtight or ventilated microclimate frame, in both cases of a totally neutral (inert), stable and controlled conditions for the paintings. In order to achieve these ideal conservation conditions for the work of art, the following points should be considered:

1. To get the volume of air inside the frame as minimal as possible by means of:

- An adequate design and appropriate materials for the manufacture and assembly of microclimate frames;
- Making the back or perimeter components of the frames narrower;
- Improving the distribution of inner elements.

2. To get the ideal balance between the inside air volume (containing the solid material of the painting: wood panel, stretcher, frame, canvas...) and the capacity of the stabilizing product (relative humidity regulator or pollution neutralizer). To stabilize the relative humidity by means of a neutral calibrated regulator.

3. An adequate insulating material keeps relative humidity stable. Fluctuations in temperature are minimized by means of the design and the materials chosen for the microclimate frame, in order to lower the effects that these fluctuations have on relative humidity.

4. Another element to be defined and solved in microclimate frame designs is the neutralization of pollutants, both in airtight and ventilated frames. Any neutralizer (either passive or active filter) must be able to be controlled, monitored, exchanged without compromising safe conditions for the work of art and it must be easy to use for the end-user museums. All microclimate frame designs avoid the use of tools which may risk or damage the work of art in the process of being assembled or maintained.

5. Microclimate frame stability must always be monitored by means of an internal mini data logger. The data should be uploaded periodically (first week every day, then in 30 days, then in 90 days and, finally, after a year). This control will enable the museums to document the quality of the environmental conditions and, if necessary, correct them in the appropriate moment.

6. To put a painting inside a microclimate frame must not be understood as a permanent protection. Using a microclimate frame involves a logical and justified follow-up, maintenance and control.

7. All materials used in microclimate frames must be laboratory tested for their suitability to be in contact with works of art (“conservation quality”).

Figure 58 shows the preparation of an integrated microclimate frame as typically performed by SIT.

Back of frame; original wood sealed with aluminium tape (left); microclimate frame hinged onto original frame (right)

Back of microclimate frame (left); panel inserted in microclimate frame and back board attached (right)

Microclimate frame sealed (left); Front of frame (right)

Figure 58: Preparation of an integrated microclimate frame (SIT).

5.5.4.2 Experience by the National Museum in Krakow

The National Museum in Krakow has tested and performed research about the functioning of three different frames, both as a partner and an end-user in the PROPAINT project. One microclimate frame was the existing enclosure for the "Lady with an ermine" by Leonardo da Vinci from the Princes' Czartoryski collection, the second a new microclimate frame, specially designed and made for "Epitaph of Jan Słupecki, deceased in 1509, Man of Sorrows and Our Lady of Sorrows" exhibited in the Bishop Erazm Ciołek Palace Department (Figure 59 - Figure 60), and the third a recently made microclimate frame without painting for tests in an accelerated ageing and climate chamber.

The criteria used for evaluating the best construction were:

- Effectiveness;
- Economy;
- Aesthetics;
- Versatility.

The general conclusions from the testing and measurements are given below:

Effectiveness

Stabilisation of the microclimate and other factors inside a microclimate frame

The influence of the microclimate frame on the stability of the environment surrounding the object has been analyzed using temperature, relative humidity and dimensional change sensors. In addition pressure change tests have been performed in order to investigate other mechanisms causing air exchange rate increases.

Data obtained show that the conditions inside the microclimate frame are very stable in spite of climate fluctuations outside the frame. Changes of the climate in the exhibition room ($\Delta T = \pm 2\ ^0C$, $\Delta RH = \pm 5$ %) are nearly completely compensated by the frame ($\Delta T = \pm 1\ ^0C$, $\Delta RH = \pm 0.5$ %, dimensional change of the painting at 0.003 %). Air pressure changes inside the microclimate frame are negligible (0.4 Pa).

At the same time it has to be mentioned that data obtained during our research of the Leonardo frame show that even an unsealed enclosure improves the stability of microclimate conditions. The test frame with a mock up panel was examined in extreme temperature and relative humidity conditions in a climate chamber in the laboratory. Even during dramatic RH changes (up to 40%) the RH inside the frame was almost stable (1-3% change) as was the panel (dimensional change in the range of 0.002%). Tested, abrupt temperature changes (of 20° C), which do not happen in real life situations, have little influence on the inside conditions ($\Delta RH = 5\%$) and on the object (dimensional change of the panel – 0.008%). Also changes of parameters during air transport were modelled ($\Delta T = -10°$ C, $\Delta RH = -30\%$) and similar satisfactory stabilizing effect of the microclimate frame was observed ($\Delta T = -10°$ C, $\Delta RH = +4\%$, dimensional change of the panel 0.006%).

Condensation of water inside a microclimate frame

In order to determine the possibility of water condensation inside the microclimate frame, measurements were performed in the frame and in the wall on which the frame was mounted. Calculating the dew point temperature one can obtain information about the possibility of water condensation on the back cover of the microclimate frame. During the whole year no condensation episodes were observed (calculated), allowing us to establish that in the tested

exhibition conditions the usage of a microclimate frame is completely safe concerning water condensation.

Corrosivity of materials used in microclimate frames
The problem of damaging effects of materials used for construction of a microclimate frame was tested using an "Oddy test" (accelerated corrosion test). Results show no corrosive effect of the environment inside the frame.

Conclusion on Effectiveness
Microclimate frames pose a barrier for fluctuations of the outside conditions during exhibition and transport. They do stabilize the direct microclimate around the painting. Moreover microclimate frames protect from dangerous mechanical damages during exhibition or travel and reduce gaseous and solid state air pollution infiltrating from the outside. Protection against vandalism and other mechanical risk is provided as well. A microclimate frame constructed from carefully selected materials may provide a low-risk environment.

Economy
The materials and assembly costs of a microclimate frame are relatively low and singular for a long period of time (in 2009 the approximate cost of one square meter of a microclimate frame using a Mirogard© Protect SCHOTT glass, did not exceed € 1000). The elaborated and checked construction scheme of our microclimate frame is repetitive for practically any object and the production can be carried out by the trained technical personnel of our museum in cooperation with our conservators. The microclimate frame is a passive solution that does not need any power feed. At the same time the stabilizing effect on the inside of the frame environment significantly reduces the need of active climate control of the exhibition rooms.

The improvement of security during exhibition and transit is achieved by the use of microclimate frames in a low-cost and low-energy way, promoting the society- and environment-friendly "Green Museum" idea at the same time.

Conclusion on Economy
Microclimate frames are an easy obtainable, cheap and a long-term solution.

Aesthetics
The construction of microclimate frames should be as close as possible to the existing historic and original frame for the protected painting. In that case the reception of the microclimate frame by visitors is brought down to a less or more visible glazing. The appropriate choice of glass used for the frame is very important. It should be non reflex, fully transparent and colourless. Following the need for visual inspection of both sides of the object (front and back) it is advised to use a transparent material for the backing (e.g. polycarbonate sheets).

It is vital to place a notice on the back of the frame informing that the enclosure is a microclimate frame and that it should not be opened - both in case of lending and during exhibition or storage in the home institution.

Conclusion on Aesthetics
The use of a microclimate frame has a low influence on the original aesthetics of the object.

Versatility

The microclimate frame construction scheme developed and tested in the National Museum in Krakow is reproducible for almost any object, while individual adaptation for different paintings is still possible. The aluminium profiles used for construction allow for spot support of panels for free dimensional changes movement of wood.

At the same time the flexibility of design makes installation of different monitoring equipment and dosimeters possible. Stable and safe mounting of dosimeters and logging devices is provided by this system.

Such a model of a microclimate frame construction allows individual modifications to suit different requirements such as formats or shapes of pictures covering simultaneously other functional uses.

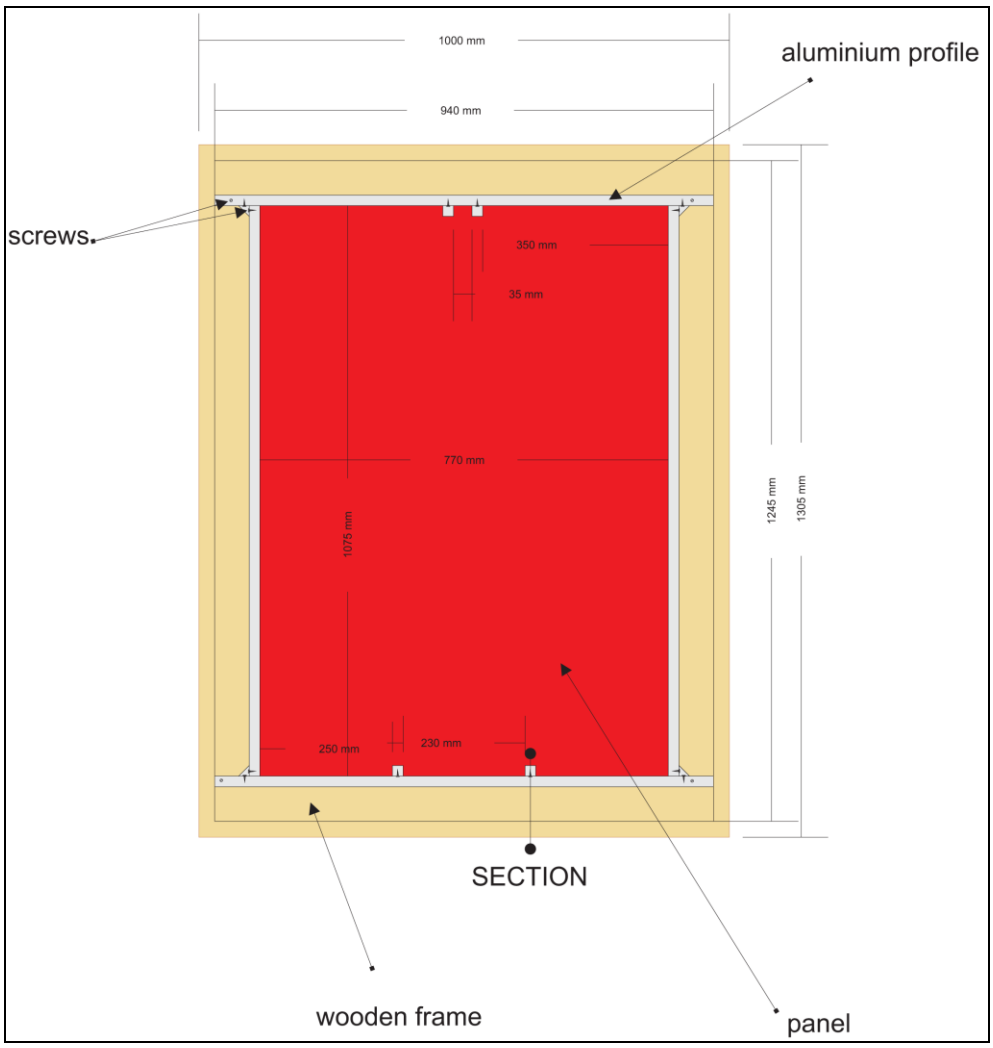


Figure 59: Microclimate frame for "Epitaph of Jan Słupecki" (back).

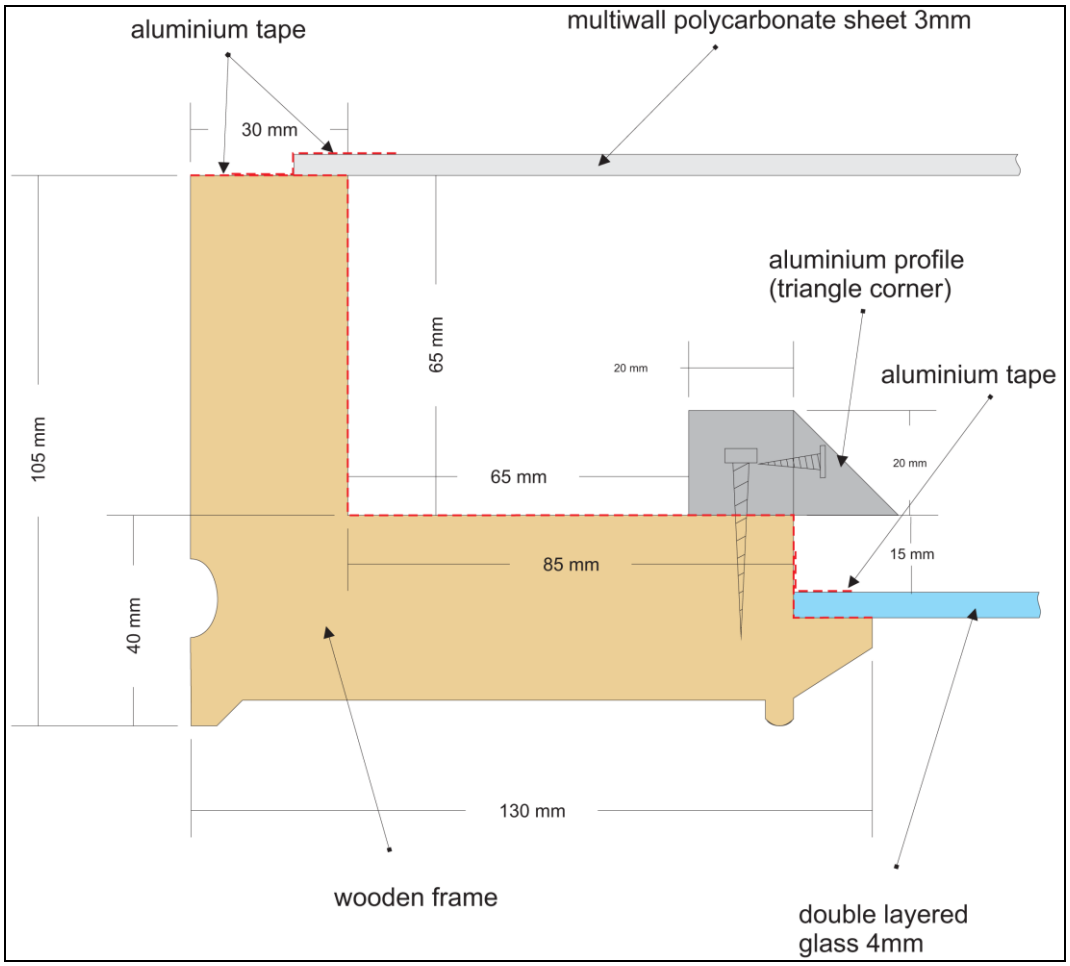


Figure 60: Microclimate frame for "epitaph of Jan Słupecki" (section).

5.5.5 Examples of microclimate frame designs

In PROPAINT four different examples of microclimate frame designs were constructed by frame builders from SIT International Transporters, The National Museum in Krakow, The National Gallery in Washington and Statens Museum for Kunst in Copenhagen, respectively. The microclimate frames were built as dummies (frame corners with painting dummies enclosed) and were also drawn as 2D (Figure 61 - Figure 64) and digital 3D models. The dummies and digital models represent typical design solutions from the four institutions and were presented to the attendants at the PROPAINT End-User Final Seminar and Workshop held in Krakow in November 2009.

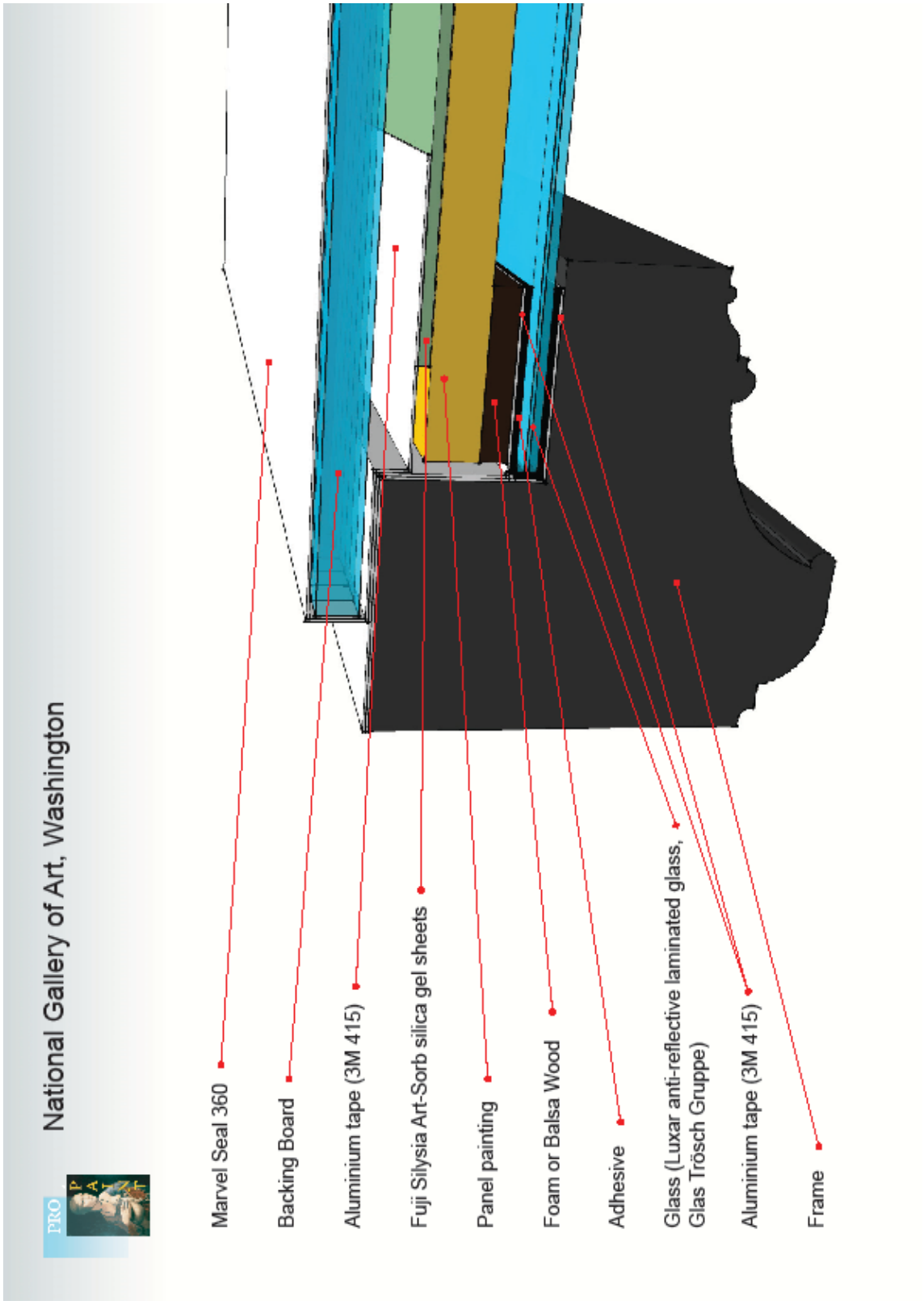


Figure 61: Microclimate frame constructed by the National Gallery in Washington.

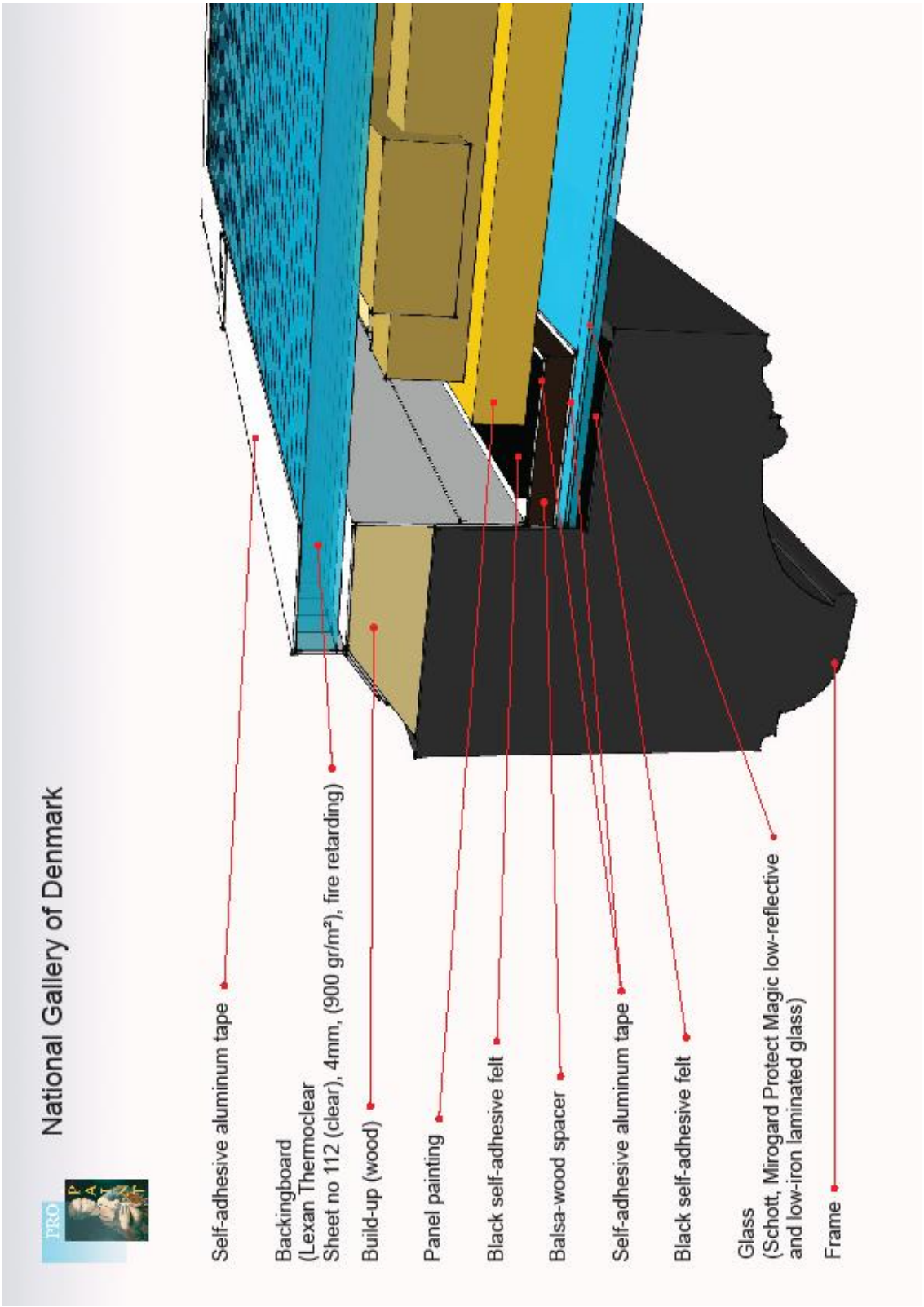


Figure 62: Microclimate frame constructed by Statens Museum for Kunst in Copenhagen.

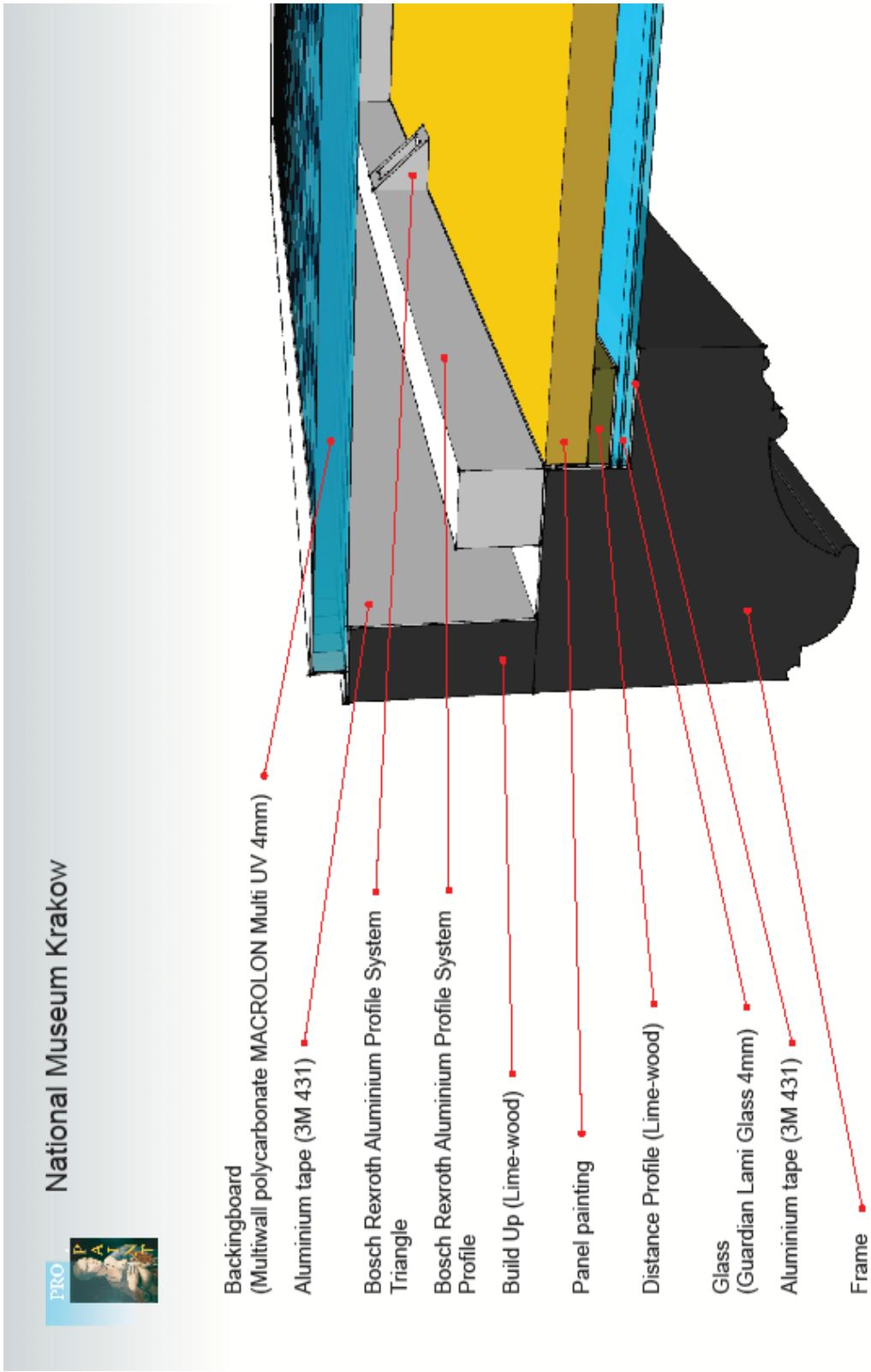


Figure 63: Microclimate frame constructed by the National Museum in Krakow.

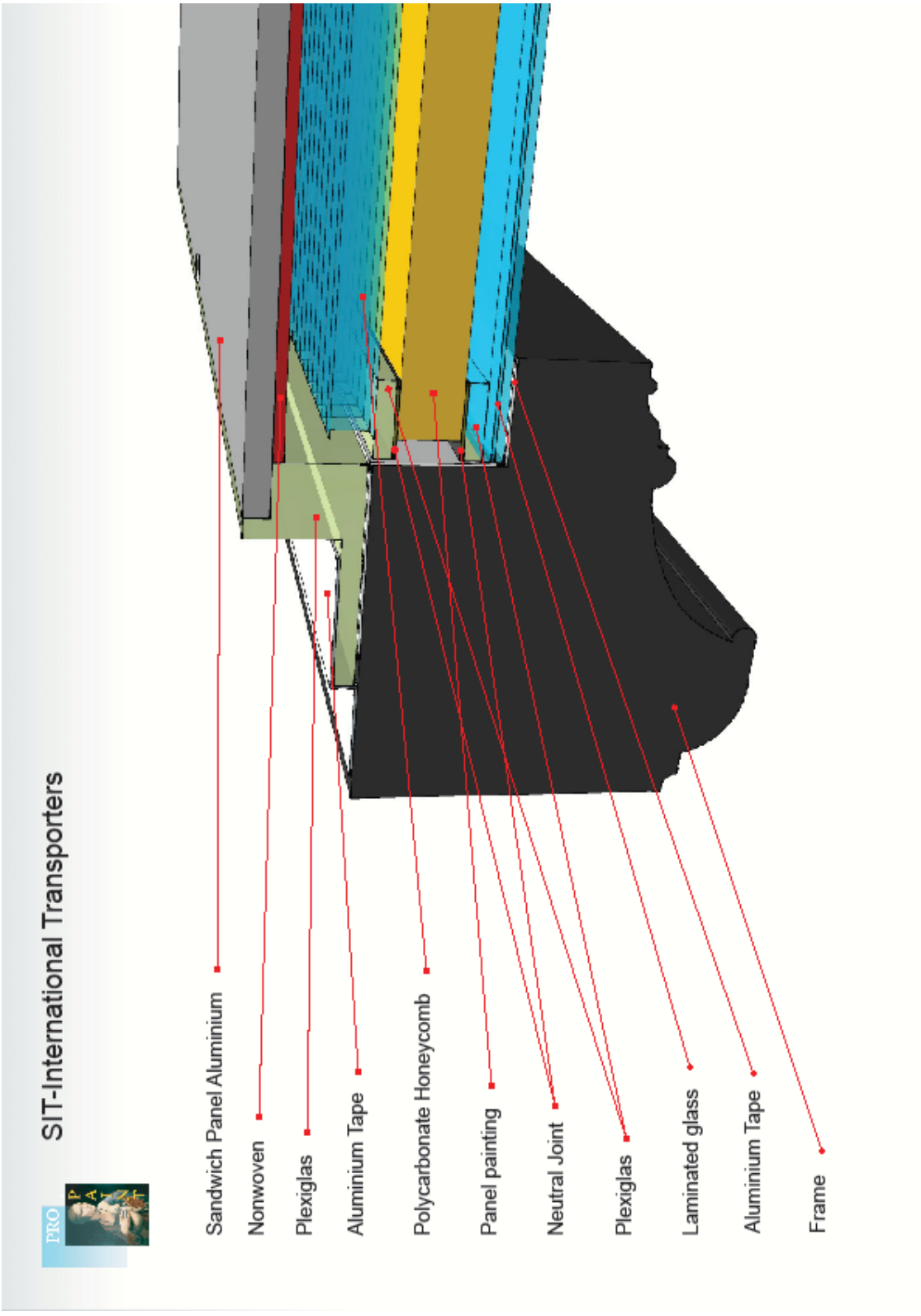


Figure 64: Microclimate frame constructed by SIT.

5.6 Modelling

Mass balance modelling was applied to study the effect of the air exchange rate and geometry of microclimate frames on the potential impact flux of gaseous air pollutants on the paintings

enclosed in the frames. The modelling was performed based on the measurements of pollutant concentrations and on the geometry and air exchange rates of the microclimate frames in the end-user museums (Table 3 and Table - 17).

The modelling indicated that the emission and deposition fluxes of light molecular weight organic acids (i.e. acetic + formic acid) were so large inside the microclimate frames, that a moderate or even quite large increase in ventilation would not be an effective mitigation measure. A hypothetical increase in the air exchange from the low values measured for the frames (no. 1, 2, 4, 9 and 13, Table 3, and Figure 23) to values of several air exchanges per hour, would (assuming that ventilation did not affect the emission rates) not significantly decrease the concentrations of the internally emitted organic acids (i.e. formic and acetic acid) and their impact fluxes to the paintings. The reason for this is the low volumes of the frames and thus small amount of pollutant removed by each single air exchange, as compared to the internal emission and deposition fluxes.

In the modelling, the "impact flux" (F_o) of oxidizing (NO_2 + O_3) and acidic (*formic acid* + *acetic acid*) gaseous pollutants to the painting was expressed by:

$$F_o(ox+ac) = F_o(NO_2 + O_3) + F_o(Form.ac + Ac.ac) \cdot C_{T1} / C_{T2} \qquad (1)$$

where C_{T1} and C_{T2} are general museum "recommended concentration levels" for "Gas 1" = (NO_2 + O_3) = 2 µg m^{-3} and "Gas 2" = (acetic acid + formic acid) = 100 µg m^{-3}, respectively (Tétreault, 2003). Any other recommended concentration levels could be used in the model calculation if found more suitable. In order to compare the modelling results for the paintings in the microclimate frames with the unprotected situation (i.e. without the microclimate frames), the impact fluxes to the paintings at the selected recommended levels were calculated for the microclimate frames and the rooms with the similar expressions (Equation 1).

To present the "impact flux" (F_o) to the painting as a function of the air exchange rate in the microclimate frame it was calculated as:

$$F_o = v_{do} \overline{C}_i \qquad (2)$$

With the average concentration inside the microclimate frame (C_i) given from:

$$\overline{C}_i = \frac{\lambda f V C_0}{\lambda V + v_{do} A_o + v_{df} A_f} + \frac{e A_e + HV}{\lambda V + v_{do} A_o + v_{df} A_f} \qquad (3)$$

Where, λ is the ventilation rate (s^{-1}), f is the frame filtration factor (dimensionless, $0 < f < 1$), C_0 and C_i are the concentrations of the pollutant gas in the room and inside the microclimate frame, respectively ($\mu g\ m^{-3}$), e is the emission rate ($\mu g\ m^{-2}\ s^{-1}$), H is the homogeneous production rate inside the frame ($\mu g\ m^{-3} s^{-1}$), v_{df} and v_{do} are the deposition velocities to the frame internal and object surfaces ($m\ s^{-1}$), respectively, A_e, A_f and A_o are the total of emitting material, microclimate frame inside and object (painting) surfaces areas (m^2), respectively, and V is the inside of microclimate frame net volume (m^3). For the internal area of the microclimate frame, A_f, the total internal frame area minus the area of the glass front was

used, as the deposition velocity of the pollutant gases to the glass was assumed to be ~ 0, as measured for inorganic gases by Grøntoft and Raychaudhuri (2004).

In Equation (2) the flux and internal concentration are calculated to be partly from infiltration, first part of Equation (3), and partly from inside of frame emission and homogeneous reaction, second part of Equation (3). Thus, possible production due to homogeneous reaction is treated similarly as emission, possible loss is treated similarly as deposition.

Assuming the same total deposition velocity to the object (painting) and microclimate frame interior ($v_{do} = v_{df}$), the surface deposition ($v_s = v_{so} = v_{sf}$) velocity was calculated from the measured values for the infiltrating gases (NO_2 and O_3) and geometry of the relatively open "Leonardo frame" (Table 3). The filtration factor (f in Equation 3) was set equal to 1 (no pollution loss in the sealing) and the filtration effect rather calculated as a transport resistance (transport limited deposition velocity) dependent on the air exchange rate:

$$v_t = \frac{\lambda}{\lambda_m}\left(\frac{1}{v_{dm}} - \frac{1}{v_s}\right)^{-1} \qquad (4)$$

Where λ_m and v_{dm} are the values for the ventilation rate and total deposition velocity calculated for each frame from the measured data, and assuming as the best approximation a linear dependence of v_t on the ventilation rate. The values for the ventilation dependent total deposition velocities, $v_d(\lambda)$, were then calculated from (Cano-Ruiz et al. 1993):

$$\frac{1}{v_d(\lambda)} = \frac{1}{v_s} + \frac{1}{v_t(\lambda)} \qquad (5)$$

From the measured values of the geometry of the microclimate frames and of the object (A_o, A_f, V), and concentration levels (C_o and C_i), the emission plus reaction rate ($eA_e + HV$) was then calculated and the change in the impact flux was subsequently estimated depending on air exchange rate (Equation 3). Besides to study the effect of varying air exchange rate, the model can also be used to study the effect of changing the frame geometry (A_f and V) assuming constant inside of microclimate frame emission rate. The possible inclusion of an absorber material can be modelled by adding an internal area equal to the absorber area (A_a) times the fraction of the deposition velocity to the absorber, to that to the frame interior (v_{da} / v_{df}).

Figure 65 shows the protection effect of the microclimate frames used in PROPAINT against air pollutants, calculated as the "impact concentration" in the room minus the "impact concentration" still remaining inside the microclimate frame. The "impact concentration" was calculated as was the flux in Equation 1, only using the measured values for the concentrations and including also SO_2 among the infiltrating gases. For the inside of the microclimate frames the infiltrating part of Equation 1, was only included for the relatively open microclimate frames at Tate Britain, Tate Store and NMK1 (Leonardo frame). For the other microclimate frames (Table 3) the modelling showed that the deposition of these gases to the painting inside the microclimate frame was ~ 0.

It is clearly seen in Figure 65 that the microclimate frames were found to be most protective against air pollutants in environments where there is high concentration of outdoor pollutants

mainly from traffic emissions (Mexico City, MNA, Oslo, NG, London, Tate B, and Valencia, MBV). In contrast, the pollution load inside the microclimate frames was found to be worse than for the unprotected (by the microclimate frame) room situation, in a more rural area (Germanic National Museum, GNM), for a room with good environmental control (Tate Store) and for a microclimate frame with high inside emission of organic acids (English Heritage, Kenwood). The SIT 1 microclimate frame was a test case with a specially constructed high emitting inside environment.

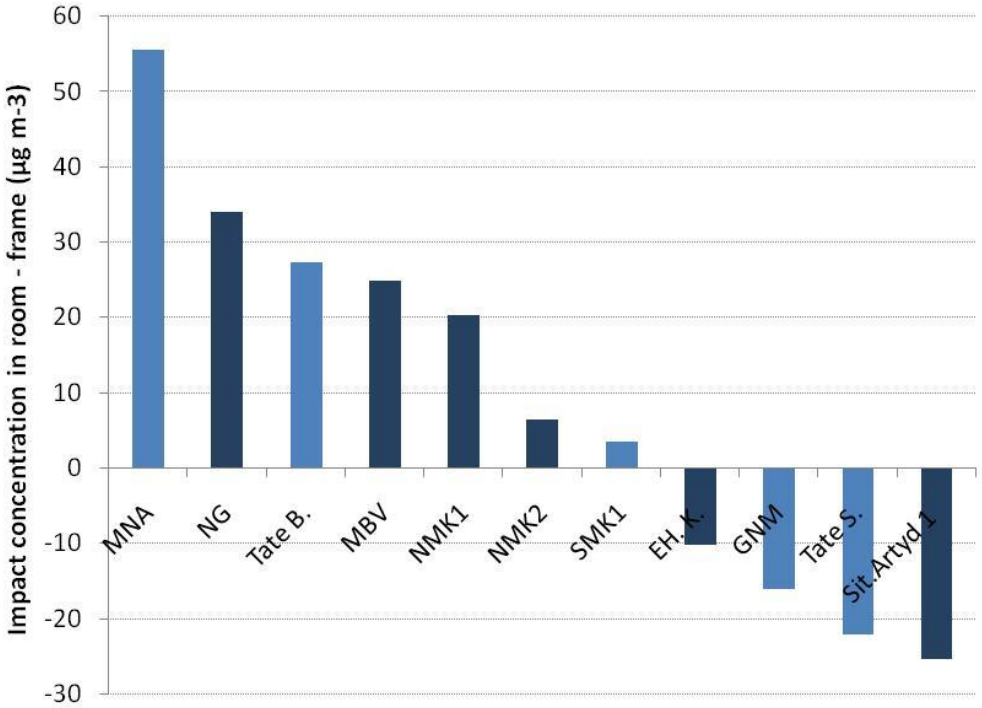


Figure 65: The protection effect against air pollutants of the microclimate frames at the end-user museums in PROPAINT, calculated as the "impact concentration" in the room minus the "impact concentration" still remaining inside the microclimate frame. (Dark blue bars are microclimate frames that were also modelled).

5.7 Standards for microclimate frames for paintings

Until now the formulation of guidelines on best practice or standards within the field of conservation has primarily been focusing on building and room scale (e.g. ASHRAE 2007; ISO 11799), or been aimed towards large collections of objects very uniform in material composition (mainly archival materials e.g.; ISO 18911; ISO 18920; BS 5454).

An end-user survey has revealed that it is presently not possible to attempt the preparation of a standard specifically on microclimate frames. A key problem, which needs to be researched further before a standard is drafted, is the effect of pollutants on the painting materials. Pollution level thresholds should be defined and systems to detect the gasses made available. The opinion amongst experts in the end-user group is that there is enough information on the general principles, but more detailed recommendations can be formulated in the future.

However, work is presently going on within the European Standardisation Organisation (CEN) under the Technical Committee 346: Conservation of Cultural property (CEN/TC 346), to set better standards for museum environments in general (CEN, 2009). One of the

working items under CEN/TC 346 contains recommendations for enclosures (showcases, microclimate frames, etc.) for art and cultural heritage objects. As a result a proposed draft of a standard for showcases was published for public enquiry on September 17, 2009:

> prEN 15999, *Conservation of cultural heritage - Guidelines for management of environmental conditions - Recommendations for showcases used for exhibition and preservation of cultural heritage.*

During the initial phase of the development of CEN work items PROPAINT partners have participated in various working groups within the CEN TC/346 and national mirror groups. The results achieved in the PROPAINT project have resulted in comments and suggestions for the new standard on showcases which has been delivered to the European Standardisation Organisation (CEN) under the Technical Committee 346: Conservation of Cultural property (CEN/TC 346).

Based on research findings within the PROPAINT project, amendments to the draft have been suggested to the Technical Committee 346 within the enquiry period. The main points of comments and suggestions include:

- To define a microclimate frame as a very special showcase in which the volume of the painting is large when compared to the volume of air inside the enclosure.

- To underline the possible need for the monitoring of the environment inside microclimate enclosures, for the effect of harmful pollutants, by the use of passive samplers, or by generic dosimeters.

- To provide better specific quantitative information on how to build an acceptable display case for a specific purpose that meets an agreed standard of protection and hence can be requested by the owner of a work of art or historic object to do a specific job of protection.

- To take into account the need of dividing the quality of microclimate enclosures into more than one level, in order to allow for the appropriate selection of a case design for a particular object or purpose. For example; possible damage from off-gassing is very much dependent on the materials contained within the display case.

- Optimally, pollution thresholds should be defined and systems to detect the gases available. A key problem, especially for microclimate frames, which needs to be researched before a standard is issued, is the effect of pollutants on painting materials.

6 Conclusion and major achievements in PROPAINT ("Benefit for users")

Environmental Measurements

- Measurements were performed for the first time of gaseous pollutants and their potential degradation impact on paintings in microclimate frames which are used to protect paintings.
- The main air pollution problem in the room locations was found to be the inorganic, mainly oxidising, species infiltrating from the outdoors. The main air pollution problem inside the microclimate frames was found to be the organic, and especially the acidic, gases emitted from materials (e.g. the frame and/or paintings).
- The EWO, GSD, RM-PQC and L-PQC dosimeters clearly have different and complementary sensitivity to the air pollutants generated externally and internally in the microclimate frames. The EWO and resin mastic coated PQCs are sensitive to inorganic and oxidizing pollutant gases typically infiltrating from outside of the frame, whereas the Glass Slide Dosimeter (GSD) and lead coated PQCs are highly sensitive to effects of organic acids typically being emitted and trapped inside the microclimate frames.
- A novel method for the evaluation of indoor (including microclimate frame) air quality for cultural heritage, by the use of combined dosimetry sensitive to both photo-oxidizing and acidic effects, was developed.
- Dosimeters were miniaturised for application inside microclimate frames and PQC dosimeters for continuous monitoring were tested and applied inside microclimate frames.
- The results from the dosimetry measurements were presented in a tolerance-location diagram, which makes the interpretation of results easy and directly relevant for conservators and other end-users responsible for indoor cultural heritage.
- Large variations of climate parameters T and RH were observed during the monitoring campaign. Higher average RH-values, but a lower range of average RH, was measured inside the microclimate frames than in the rooms, showing the buffering effect of the frames. Temperature and relative humidity variation can affect negatively the preservation of cultural heritage objects. Consequently, even though the dosimeters are sensitive to the climate factors, it is highly recommendable to perform separate climate monitoring.
- Inorganic oxidizing compounds were detected in low concentrations inside the microclimate frames whereas high concentrations were measured in the rooms. The study has demonstrated the protective effects of microclimate frames for paintings against externally generated pollutants.
- In contrast, high levels of VOCs such as acetic and formic acid, toluene, p- and m-xylenes, α-pinene, limonene and 3-carene were detected inside the microclimate frames. The high concentration of some of these VOCs inside microclimate frames may be harmful for enclosed paintings. α-pinene and limonene may react with infiltrating oxidizing agents and will result in secondary production of VOCs such as formic and acetic acid, aldehydes and fatty acids.

- More research on the impact of organic compounds, and particularly of organic acids, on paintings needs to be performed. Better informed recommended levels for specific organic compounds and their effects on paintings need to be established.

Varnishes

- It was found that the investigated pollutants, NO_2, O_3 and acetic acid, have an effect on the degradation of natural resins, indicating that light is not the only factor that must be taken into account to preserve the varnishes/paintings.
- For the first time the effect of acetic acid on natural resins was tested. The results showed that this pollutant has oxidising and cross linking power which seems comparable to that of NO_2 and O_3.
- It was shown that pollutant doses inside microclimate frames can be different from those outside microclimate frames, and in particular organic components, such as acetic acid, can have high concentrations (giving large doses) inside the frames. The analysis performed of varnishes that were exposed to museum environments, both outside and inside microclimate frames, revealed that the microclimatic frame does not necessarily act as a protection against oxidation and cross linking of natural resin, in the short time scale (1-2 years).
- The studies confirmed that the investigated synthetic resins, Paraloid B 72 and MS2A, are, from a molecular point of view, less prone to oxidation than natural resins.
- For the first time the detailed chemical composition of MS2A resin was revealed, highlighting the effect of artificial and natural ageing on physical chemical properties of the resin, also when Tinuvin 292 was added as stabiliser.
- The research in PROPAINT showed that solvents used in the application of varnishes can be trapped for very long time in the varnish layer. This was the case for the MS2A varnishes, in which the aromatic components of the solvent used for the varnish preparation were retained in the varnish film, even two years after the preparation. The aromatic compounds are known to be dangerous for the human health and may also be harmful for the paint layers, because they could migrate towards the paint films and act as solvents for some of the paint constituents. This could affect the stability of paint layers, and contribute to the well known phenomenon of the ghost images.

Microclimate frames

- Dosimeter systems for the generic measurement of pollution and climate effects on materials/cultural heritage objects were adapted for use inside microclimate frames, - to evaluate the environmental impact on paintings.
- The measurement of the environments inside microclimate frames for paintings and of the physical characteristics of the microclimate frames, such as air exchange and internal dimensions, provided improved knowledge about preservation conditions in microclimate frames and about the required design and performance of the microclimate frames.
- The improved knowledge about the required design and performance of microclimate frames obtained during the PROPAINT project will contribute to a higher standard within preventive conservation of paintings in display, transit or storage.
- By testing of existing and new-built microclimate frames in different end-user locations and in the laboratory, performance criteria related to microclimate frames were defined, including investigation of mitigation methods to solve the problem of internal pollutant emissions inside the frames.
- A decision making model for the design of microclimate frames was created. The model can function as a general guideline for conservators when considering which parameters will influence the quality of a microclimate frame.

- A mathematical model for calculating pollution "impact" fluxes to paintings in microclimate frames as compared to the unprotected situation and to recommended levels was developed. The model can be used to study the effect of air exchange and frame geometry (internal volume and area of the frame) on the deposition "impact" fluxes.
- The results achieved in the PROPAINT project have furthermore resulted in a number of comments and suggestions for a new standard on showcases, which is currently written by the European Standardisation Organisation (CEN).

Future research needs:

The results obtained in PROPAINT have put the focus on remaining questions that needs to be investigated in relation to preventive conservation of paintings by the use of microclimate frames.

- Many different volatile organic compounds (VOCs) were detected inside the microclimate frames, many in high concentrations. Little is known about the degradation effects of the VOCs on cultural heritage objects made from organic materials, such as paintings. There is some evidence of degradation impact of the light molecular weight organic acids (i.e. acetic and formic acid) that are expected to be among the most aggressive organic compounds. However, it is unknown if solvents such as toluene that is often present and chloroform, which can be present, inside microclimate frames are degrading. More research needs to be performed to establish which degradation effects organic acids and other VOCs have on diverse organic materials in cultural heritage objects. This research should include continued investigation of effects on varnishes and paintings generally. More study of especially acetic acid effects on varnishes and paintings, including old varnish and paint layers, should be performed.

- It is important to investigate further the effect and practical applicability of different mitigation measures to reduce the concentrations (and thus potential degradation impact) of organic contaminants inside microclimate frames. Mitigation measures can be application of absorbing materials, installation of barrier films to cover construction materials, such as wood, that emits pollutant gases, or changing of the composition of the atmospheres inside the microclimate frames. It is important both to understand how such measures work and how they can be applied in the most practical and economical manner. This research should include improvement of frame design to include new mitigation measures.

- There is still room and need for technical improvement and refinement of measurement methods, and especially in making these technologies as practically available and affordable as possible to conservators and other people responsible for the preservation of paintings. This should include devices for in situ and/or continuous and/or on-line results measurements.

7 Dissemination, exploitation and use of results

The PROPAINT project has been active in producing exploitable results and in disseminating new knowledge resulting from its work. Major achievements that are already in the process of being exploited in the conservation market are the development of techniques and methodology for a more complete dosimetry of indoor and microclimate environments to improve cultural heritage preservation. This exploitation is assisted by reference results from measurements obtained in PROPAINT. These results have improved both the calibration of dosimeter measurements against environmental parameters and the inter-comparison of measurement methods for their practical combination and usefulness for evaluation of impact on real objects in the field.

Another major achievement is the improved understanding of the conditions for the design of optimal microclimate frames for the protection of paintings. This work has already influenced the partners to modify their practice of design and building of mc-frames to improve the frames.

PROPAINT has also investigated how varnishes protect paintings. The results obtained in this complicated field of investigation are important to understand how the use of microclimate frames can affect the environmental degradation impact on varnished paintings, and the longer term exploitation in conservation practical is potentially very important.

A considerable effort has been made to disseminate results to the cultural heritage and conservation community beyond the PROPAINT partnership to maximize the impact both in terms of exploitation of results in the market and to improve work practices in institutions. The dissemination activities carried out during the PROPAINT project have all been directed to enhance the exploitation of results in the diverse ways of their usage. - The publication effort is still ongoing.

8 References

Ashley-Smith, J. and Moncrieff, A.J. (1984) Experience with silica gel for controlling humidity in show cases. In: *ICOM Committee for Conservation 7th Triennial Meeting, Copenhagen, 10-14 September 1984, Preprints.* Ed. by: Diana de Froment, vol. 2, 84.17.1-5. Paris, ICOM Committee for Conservation.

ASHRAE (2007) Chapter 21: Museum, galleries, archives and libraries. In: *ASHRAE Handbook, HVAC Applications.* Ed. by: Mark Owen. Atlanta, GA, American Society of Heating, Refrigerating, and Air Conditioning Engineers, Inc.

Atkins, P.W. (1998) Physical chemistry. Sixth edition. Oxford, Oxford University Press.

Bacci, M., Cucci, C., Dupont, A.-L., Lavédrine, B., Picollo, M. and Porcinai, S. (2003) Disposable indicators for monitoring lighting conditions in museums. *Env. Sci. Technol., 37*, 5687-5694.

Bacon, L. and Martin. G. (2000) Out of Africa! Display case strategies - the theory and the reality. In: *Tradition and innovation: advances in conservation. Preprints IIC Melbourne Conference.* Ed. by: Roy, A. and Smith, P. London, International Institute of Conservation. pp. 18-23.

Bülow, A.E., Watt, D.S. and Colston, B.J. (2003) Microenvironments within glass-fronted book cases : a study comparing environmental changes within books and interactions with local environments. *Papier Restaurierung, 4*, 23-31.

Boddi, R., Camera, P., Danti, C. and Sciurpi, F. (1999) Testing of a museum showcase equipped with an active and passive system for control of internal hygrometric conditions. In: *Art 99, 6th international conference on non-destructive testings and microanalyses for the diagnostics and conservation of the cultural heritage*. Rome, Euroma, pp. 1953-1968.

Bosshard, E. (1990) Klimavitrinen für Gemälde, Eine wirksame un äestetisch befriedigende Methode. *Restauro, 3*, 176-180.

Bosshard, E. and Richard, M. (1989) Climatized vitrines for paintings: An uncomplicated but efficient method. In: *American Institute for Conservation: Annual Meeting Preprints, Cincinnati.* Washington, American Institute for Conservation.

Bullock, L. and Saunders, D. (1999) Measurement of cumulative exposure using Blue Wool standards. In: *ICOM-CC 12th Triennial, Lyon*. Ed. by: J. Bridgland. London, James and James. pp. 21–26.

Calver, A., Halbrook, A., Thickett, D. and Weintraub, S. (2005) Simple methods to measure air exchange rates and detect leaks in display and storage enclosures. In: *ICOM 14th Triennial meeting, The Hague, 12-16 September 2005, ICOM Committee for Conservation, Preprints, Volume II*. pp. 597 - 609.

Camuffo, D. (2000) Microclimate for cultural heritage. Amsterdam, Elsevier. (Developments in atmospheric science, 23).

Camuffo, D., Sturaro, G. and Valentino, A. (2000) Showcases: a really effective mean for protecting artworks? *Thermochim. Acta, 365*, 65-77.

Cano-Ruiz, J.A., Kong, D., Balas, R.B. and Nazaroff, W.W. (1993) Removal of reactive gases at indoor surfaces. Combining mass transport and surface kinetics. *Atmos. Environ., 27 A*, 2039-2050.

Carrió, V. and Stevenson, S. (2003) Assessment of materials used for anoxic microenvironments. In: *Conservation Science 2002. Papers from the conference held in Edinburgh, Scotland 22-24 May 2002*. London, Archetype. pp. 32-38.

Cassar, M. (1988) A microclimate within a frame for a portrait hung in a public place. In: *United Kingdom Institute for Conservation 30th Anniversary Conference Preprints*, compiled by Victoria Todd. London, United Kingdom Institute for Conservation, pp. 46-49.

Cavicchioli, A. (1996) Chemical sensors for indoor environment. Thesis, M.Sc Analytical Chemistry. Birkbeck College, University of London.

Chiantore, O., Trossarelli, L. and Lazzari, M. (2000) Photooxidative degradation of acrylic and methacrylic polymers. *Polymer, 41,* 1657-1668.

Christopher, A., Maines, E. and de la Rie, E.R. (2005) Size exclusion chromatography and differential scanning calorimetry of low molecular weight resins used as varnishes for paintings. *Progr. Org. Coating, 52,* 5239-45.

Colombini, M.P. and Modugno, F. (2009) Organic mass spectrometry in art and archaeology. Chichester, Wiley.

Colombini, M.P. and Tassi, L. (eds.) (2008) New trends in analytical, environmental and cultural heritage chemistry. Research Signpost, Transworld Research Network, Kerala, India.

Cruz, A.J., Pires, J., Carvalho, A.P. and Brotas de Carvalho, M. (2008) Comparison of adsorbent materials for acetic acid removal in showcases. *J. Cult. Herit., 9*, 244-252.

Dahlin, E., Grøntoft, T., Rentmester, S., Calnan, C., Czop, J., Hallet, D., Pitzen, C. and Sommer-Larsen, A. (2005) Development of an early warning sensor for assessing deterioration of organic materials indoor in museums, historic buildings and archives In: *ICOM 14th Triennial meeting, The Hague, 12-16 September 2005, ICOM Committee for Conservation, Preprints, Volume II*. pp. 617-624.

de la Rie, E.R. and Shedrinsky, A.M. (1989) The chemistry of ketone resins and the synthesis of a derivative with increased stability and flexibility. *Stud. Conservat., 34*, 9-19.

de la Rie, E.R. (1987) The influence of varnishes on the appearance of paintings. *Stud. Conservat., 32*, 1-13.

de la Rie, E.R. (1989) Old master paintings: a study of the varnish problem. *Analyt. Chem., 61*, 1228A-1240A.

Di Pietro, G. and Ligterink, F.J. (1999) Prediction of the relative humidity response of backbord-protected canvas paintings. *Stud. Conservat., 44*, 269-277.

Diamond, M. (1974) A micro-micro-climate. *Museums J., 4*, 161-163.

Dietemann, P., Edelmann, M.J., Meisterhans, C., Pfeiffer, C., Zumbuhl, S., Knochenmuss, R. and Zenobi, R. (2000) Artificial photoaging of triterpenes studied by graphite-assisted laser desorption/ionization mass spectrometry. *Helv. Chim. Acta, 83*, 1766-1777.

Dietemann, P. (2003) Towards more stable natural resin varnishes for paintings, PhD Thesis. Zurich, ETH Zurich (Diss., Naturwissenschaften ETH Zürich, Nr. 15224).

Dietemann,P., Higgitt,C., Kalin, M., Edelmann,M.J., Knochenmuss,T. and Zenobi, R. (2009) Ageing and yellowing of triterpenoid varnishes-the Infouence of aging conditions and resin composition. *J. Cult. Herit., 10*, 30-40.

Dohety, T., Metro, B. and Gomez, R. (2008) The transport and display of icons from Saint Catherine's monastery. In: *Conservation and Access: Contributions to the 2008 IIC Congress, London.* London, IIC. pp. 50-55.

Dupont, A-L and Tétreault J. (2000) Cellulose degradation in an acetic acid environment. *Stud. Conservat., 45*, 201-210.

Edmunds, S. (1988) A microclimate box for a panel painting fitted within the frame. In: *United Kingdom Institute for Conservation 30th Anniversary Conference Preprints*, compiled by Victoria Todd. London, United Kingdom Institute for Conservation. pp. 50-53.

Ferm, M. (1991) A sensitive diffusional sampler. Stockholm, Swedish Environmental Research Institute (IVL B-1020).

Gettens, R.J. and Stout. G.L. (1966) Painting materials: A short encyclopaedia. 2d ed. New York, Dover Publications.

Gilberg, M. (1990) Inert atmosphere disinfestation using ageless oxygen scavenger. In: *ICOM Committee for Conservation 9th Triennial Meeting Dresden, German Democratic Republic, 26-31 August 1990, Preprints.* Ed. by: Kirsten Grimstad, vol. 2. Los Angeles, ICOM Committee for Conservation. pp. 812-816

Godoi, R.H.M., Kontozova, V., Godoi, A.F.L. and Grieken, R. van (2004) Investigation of individual particles and gaseous air pollutants in showcases. In: *Air pollution and cultural heritage. Proceedings of the international workshop on air pollution and cultural heritage, 1-3 December 2003, Seville, Spain.* Ed. by: Saiz-Jimenez, C. London, Taylor & Francis. pp. 147-150.

Grøntoft, T. and Raychaudhuri, M.R. (2004) Compilation of tables of surface deposition velocities for O_3, NO_2 and SO_2 to a range of indoor surfaces. *Atmos. Environ., 38*, 533-544.

Grøntoft, T., Dahlin, E., Henriksen, J.F., Rentmeiseter, S., Hanko, M., Heinze, J., Taylor, J., Blades, N. and Cassar, M. (2006) An early warning system for organic materials in

museums, historic buildings and archives. In: *Safeguarded cultural heritage : understanding and viability for the enlarged Europe. Proceedings of the 7th European conference "Sauveur", Prague, Czech Republic, 2006.* Ed. by Milos Drdácký, Michel Chapuis, co-ed. M. Cassar, E. Dahlin et al. Praha, ITAM. pp. 41-50.

Grøntoft, T., Henriksen J. F., Dahlin, E., Lazaridis, M., Czop, J., Sommer-Larsen, A., Hallett, K., Calnan, C., Pitzen, C. and Cassar, J.A. (2005) Sensor and environmental data from the field test programme. EU project MASTER (EVK4-CT-2002-00093) Deliverable no. D. 3.1, WP 3.

Hackney S.J., and Hedley, G.A. (1984) Measurements of the ageing of linen canvas. *Stud. Conservat., 26*, 1-14.

Hackney, S. (1987) The dimensional stability of paintings in transit. In: *ICOM Committee for Conservation 8th Triennial Meeting, Sydney, Australia, 6-11 September 1987, Preprints.* Ed. by: Kirsten Grimstad, vol. 2. Marina del Rey, CA, Getty Conservation Institute. pp. 597-600.

Hackney, S. (1990) Framing for conservation at the Tate Gallery. *Conservator, no. 14*, 44-52.

Hackney, S. (2007) The Evolution of a conservation framing policy at Tate. In: Museum Microclimates: *Contributions to the Copenhagen conference, 19-23 November 2007*. Ed. by: Padfield, T. and Borchersen, K. Copenhagen, National Museum of Denmark. pp. 229-235.

Hahn, O., Wilke, O. and Jann, O. (2007) Indoor air quality in show cases - an attempt to standardise emission measurements. *Z. Kunsttechnol. Konserv., 21,* 275-279.

Hatchfield, P. (2002) Pollutants in the museum environment - Practical strategies for problem solving in design, exhibition and storage. London, Archetype.

Holmberg, J.G. and Kippes, W. (2003) Improvement of showcase environment at the Silberkammer, Vienna. In: *Conservation science 2002: papers from the conference held in Edinburgh, Scotland 22-24 May 2002.* Ed. By: Townsend, J.H., Eremin, K. and Adriaens, A. London, Archetype. pp. 25-31.

Kampa, N. (2000) Toward standardization of a high-performance display case. Presented at: Tradition and innovation: advances in conservation, IIC Melbourne Congress 2000 (Poster).

Kenjo, T. and Toishi, K. (1975) Purification of air with zeolite. *Sci. Conserv., 12,* 27-31.

Knight, P. (1983) An enclosure for the Tate Panels in the Church of All Hallows Berkyngechirche by the Tower. *Conservator, 7,* 34-36.

Knop, A., Banik, G., Schade, U. and Brchle, I. (2007) Paper and board in closed boxes: alteration of water sorption capacity during cyclic temperature changes. *Restaurator, 28,* 218-223.

Lambert, F.L., Daniel, V. and Preusser, F.D. (1992) The rate of absorption of oxygen by Ageless: The utility of an oxygen scavenger in sealed cases. *Studies Conserv., 37,* 267-274.

Larsen, R. (Ed.) (1996) Deterioration and conservation of vegetable tanned leather. Environment leather project, Contract No EV5V-CT94-0514. Copenhagen, European Comission (Research report/Protection and conservation of European cultural heritage, No. 6).

Larsen, R. (ed.) (2007) Improved damage assessment of parchment, IDAP: assessment, data collection and sharing of knowledge. Luxembourg, Office for Official Publications of the European Communities (EUR 22838 EN).

Lazzari, M. and Chiantore, O. (2000) Thermal aging of paraloid acrylic protective polymers. *Polymer, 41,* 6447-6455.

Leissner, J, Beuschlein, S., Pilz, M., Martin, G., Blades, N. and Redol, P. (1996) Assessment and monitoring the environment of cultural property. Final report 1993-1996. Brussels, EC Environment Programme (Contract number EV5V-CT92-0144 AMECP).

López-Aparicio, S., Grøntoft, T., Dahlin, E., Odlyha, M. and Mottner, P. (2009) EU project PROPAINT (FP6 SSPI n^{o} 044254). Deliverable D 1.2. Final results for environmental conditions observed for paintings in microclimate frames based on dosimeter and other measuring techniques in selected case studies.

Maekawa, S. (ed.) (1998) Oxygen-free museum cases. Los Angeles, Getty Conservation Institute (Research in Conservation).

Maish, J., Maekawa, S. and Elert, K. (1999) Preliminary evaluation of compressed air membrane dryers for exhibit case desiccation. *Stud. Conserv., 44,* 104-112.

MASTER project (2009) Preventive conservation strategies for protection of organic objects in museums, historic buildings and archives (EVK4-CT-2002-00093).
URL: http://www.nilu.no/master/.

Mecklenburg, M.F. (2007) Micro climates and moisture induced damage to paintings. In: *Museum microclimates, Copenhagen, November 2007: Contributions.* Ed. by: Padfield, T. and Borchersen, K.. Copenhagen, National Museum of Denmark. pp. 19-25.

McPail, D., Lam, E. and Doyle, A. (2003) The heat sealing of ESCAL barrier films. *Conservator, 27,* 107-116.

Mills, J. and White, R. (1999) Organic chemistry of museum objects. Oxford, Butterworth-Heinemann.

Mottner, P. (2007) Early warning dosimeters for monitoring indoor museum climate: Environmental impact sensors and lightcheck^{TM}. (2007) In: *Strategies for Saving our Cultural Heritage. Papers presented at the CSSIM / ICOM-LIC Meeting, Cairo, 25 February - 1 March 2007.* Ed. by: Argyropoulos, V., Hein, A. and Abdel-Harith, M. TEI of Athens.

Mottner, P. (2006) Early warning dosimeters for monitoring indoor museum climate: Environmental impact sensors and lightcheck^{TM}. Presented at the 7th Indoor Air Quality (IAQ), Braunschweg, November 15-16, 2006.
URL: http://iaq.dk/iap/iaq2006/Mottner_IAQ2006.pdf.

Newnham, M. (2002) Ventilated film cans - their effect on the diffusion of decomposition by-products from motion picture film. *SMPTE Journal, 111,* 29-33.

Norton, C. and Furuhata, S. (2006) Passepartout : properties, performance, packing: reevaluation of an environmental package for travelling works of art on paper. *The Book and Paper Group Annual, 25,* 29-33.

Oddy, W.A. (1973) An unsuspected danger in display. *Mus. J., 73,* 27-28.

Odlyha, M., Cohen, N.S., Campana, R. and Foster, G.M. (2000) Environmental research for art conservation and assessment of indoor conditions surrounding cultural objects. In: *Art et chimie, la couleur: actes du congrés, Paris 16-18 Septembre, 1998.* Paris, CRNS. pp. 163-168.

Odlyha, M., Wade, N., Wang, Q., Campana, R., Slater. J.M., Ormsby, B., Rhyl Svendsen, M., Padfield, T., De Santis, F., Smith, V.A., Bullock, L., Ferreira, E.S.B., Boon, J.J. and Pratt, K. (2005a) Microclimate indoor monitoring: damage assessment for cultural heritage preservation. In: *14th Triennial meeting, The Hague, 12-16 September 2005, ICOM Committee for Conservation, Preprints, Volume II.* pp. 670-676.

Odlyha, M., Groot, J.d., Bozec, L., Horton, M.A., Masic, A. and Coluccia, S. (2005b) Damage assessment of parchment by micro-thermal analysis and scanning electron microscopy. In: *14th Triennial meeting, The Hague, 12-16 September 2005, ICOM Committee for Conservation, Preprints, Volume II*. pp. 759-765.

Odlyha, M., Theodorakopoulos, C., Thichet, D., Ryhl-Svendsen, M., Slater, J.M., Campana, R. (2007) Dosimeters for indoor microclimate monitoring for cultural heritage. In: *Museum Microclimates: Contributions to the Copenhagen conference, 19-23 November 2007*. Ed. by: Padfield, T. and Borchersen, K.. Copenhagen, National Museum of Denmark. pp. 73-79.

Ohe S. (2009) Computer aided data book of vapor pressure. Second edition. Tokyo, Data Book Publishing. URL: http://e-data.jp/vpcal1/e/

Oosten, T.B. van (2002) Crystals and crazes: degradation in plastics due to microclimates. In: *Plastics in art: history, technology, preservation*. Ed. by: Oosten, T. van, Shashous, Y, and Waentig, F. München, Siegl (Kölner Beiträge zur Restaurierung und Konservierung von Kunst- und Kulturgut, 15). pp. 80-89.

Osete-Cortina, L. and Domenech-Carbò, M.T. (2006), Characterization of acrylic resins used for restoration of artworks by pyrolysis-silylation-gas chromatography/mass spectrometry with hexamethyldisilazane. *J. Chromatogr. A, 1127,* 228–236.

Padfield, T. (1966) The control of relative humidity and air pollution in show-cases and picture frames. *Stud. Conserv., 1,* 8-30.

Padfield, T., Berg, H., Dahlstrom, N. and Rischel, A-G. (2002) How to protect glazed pictures from climatic insult. In: *Preprints of the 13rd Triennial Meeting, Rio de Janeiro, 22 - 27 September 2002*. London, James and James. pp. 80-85.

Pinna, D., Galeotti, M., Mazzeo, R. (eds.) (2009) Scientific examination for the investigation of paintings. A handbook for conservator-restorers. Firenze, Centro Di della Edifimi srl.

Ramer, B.L. (1984) The design and construction of two humidity-controlled display cases. In: *ICOM Committee for Conservation 7th Triennial Meeting, Copenhagen, 10-14 September 1984, Preprints*. Ed. by: Diana de Froment, vol. 2, 84.17.46-49. Paris, ICOM Committee for Conservation.

Richards, M. (1994) The transport of paintings in microclimate display cases. In: *Preprints of the contributions to the Ottawa Congress, 12-16 September 1994: Preventive conservation-practice, theory and research*. Ed. by Roy, A. and Smith, P. London, IIC. pp. 185-189.

Richards, M. (2007) The benefits and disadvantages of adding silica gel to microclimate packages for panel paintings. In: *Museum Microclimates: Contributions to the Copenhagen conference, 19-23 November 2007*. Ed. by: Padfield, T. and Borchersen, K. Copenhagen, National Museum of Denmark. pp. 237-244.

Routledge, V, (2000) The development of MS2A reduced ketone resin in painting conservation. *WAAC, 22*.

Ryhl-Svendsen, M. (2006) Indoor air pollution in museums: a review of prediction models and control strategies. *Rev. Conserv., 7,* 27-41.

Ryhl-Svendsen, M. (2008) Corrosivity measurements of indoor museum environments using lead coupons as dosimeters. *J. Cult. Herit., 9,* 285-293.

Ryhl-Svendsen, M., Grøntoft, T., Dahlin, E., Lopez-Aparicio, S., Odlyha, M., Mottner, P., Scharff, M., Andrade, G., Obarazanowski, M., Czop, J., Hackney, S., Thickett, D., Wadum, J., Colombini, M.P. and Bonaducci, I. (2009) Gaseous pollutants inside microclimate-frames: results from the PROPAINT project. In: *Contributions to the symposium Facing the challenges of panel paintings conservation: Trends, treatments and training, Los Angeles, May 17-18, 2009*. Los Angeles, Getty Conservation Institute (submitted).

Sack, S.P. and Stolow, N. (1978) A micro-climate for a Fayum painting. *Stud. Conserv., 23,* 47-56.

Scalarone, D., Duursma, M.C., Boon, J.J. and Chiantore, O. (2005) MALDI-TOF mass spectrometry on cellulosic surfaces of fresh and photo-aged di- and triterpenoid varnish resins. *J. Mass Spectrom., 40,* 1527–1535.

Schieweck, A., Markewitz, D. and Salthammer, T. (2007a) Screening emission analysis of construction materials and evaluation of airborne pollutants in newly constructed display cases. In: *Museum Microclimates: Contributions to the Copenhagen conference, 19-23 November 2007*. Ed. by: Padfield, T. and Borchersen, K.. Copenhagen, National Museum

of Denmark. pp. 67-72.

Schieweck, A., Markewitz, D. and Salthammer, T. (2007b) Chemical substances in newly constructed showcases. *Z. Kunsttechnol. Konserv., 21*, 280-286.

Sebera, D. (1994) Isoperms: an environmental tool. Washington, Committee on Preservation and Access.

SENSORGAN project (2009) Sensor system for detection of harmful environments for pipe organs. Contract no. 022695. URL: http://goart.gu.se/cgi-bin/senslev1/sensorgan.taf

Shashoua, Y. (1999). Ageless oxygen absorber: from theory to practice. In: *Preprints of the 12th Triennial Meeting, Lyon, 29 August - 3 September 1999.* Ed. by: Bridgland, J. and Brown, J. London, James and James. pp. 881-887.

Shiner, J. (2007) Trends in microclimate control of museum display cases. In: *Museum Microclimates: Contributions to the Copenhagen conference, 19-23 November 2007*. Ed. by: Padfield, T. and Borchersen, K. Copenhagen, National Museum of Denmark. pp. 267-275.

Simpson, W.S. (1893) An improved method of means of preserving oil paintings, water colour drawings, engravings, photographs, prints, and printed matter from atmospherical deterioration and from decay. London, H.M. Stationary Office.

Sobeih, K. L., Baron, M. and Gonzalez-Rodriguez, J. (2008) Recent trends and developments in pyrolysis–gas chromatography. *J. Chromatogr. A, 1186*, 51-66.

Sozzani, L. (1992) Climate vitrine for paintings using the picture's frame as primary housing. Unpublished report in the Conservation Department of the Rijksmuseum, Amsterdam.

Stolow, N. (1965) Report on controlled environment for works of art in transit. Presented at the joint meeting of the ICOM Committee for Scientific Museum Laboratories and the ICOM Sub-Committee for the Care of Paintings, Washington & New York, September 1965. Ottawa, Stolow.

Stolow, N. (1967) Standards for the care of works of art in transit. In: *Contributions to the London Conference on Museum Climatology, 18-23 September, 1967*. London, IIC. pp. 271-284.

Strlič M. (2009) Personal communication in the EU project TeACH (URL: http://www.teach-project.eu/).

Svare, S. and Lyng Petersen, R. (2000) Professional notes conservation: climate-conditioned display case for Lorich's map of the Elbe in the Hamburg Public Records Office. *Mus. Manag. Curatorship, 18*, 193-204.

Theodorakopoulos, C., Boon, J.J. and Zafiropulos, V. (2009) Direct temperature mass spectrometric study on the depth-dependent compositional gradients of aged triterpenoid varnishes. *Int. J. Mass Spectrom., 284*, 98-107.

Tétreault, J. (2003a) Guidelines for pollutant concentrations in museums. *CCI newsletter, 31*, 3-5.

Tétreault, J. (2003b) Airborne pollutants in museums, galleries, and archives*:* Risk assessment, control strategies and preservation management. Ottawa, Canadian Conservation Institute.

Thickett, D. (2005) Print frame microclimates. In: *Art on paper: mounting and housing*. Ed. by: Rayner, J., Kosek, J.M. and Christensen, B. London, Archetype. pp. 48-54.

Thickett, D., David, F. and Luxford, N. (2005) Air exchange rate - the dominant parameter for preventive conservation? *Conservator, 29:6,* 19-34.

Thickett, D., Fletcher, P., Calver, A. and Lambarth, S. (2007) The effect of air tightness on RH buffering and control. In: *Museum Microclimates: Contributions to the Copenhagen conference, 19-23 November 2007*. Ed. by: Padfield, T. and Borchersen, K. Copenhagen, National Museum of Denmark. pp. 245 -252.

Thomson, G. (1961) Museum climate: Humidity control, packing and transport. *Stud. Conserv., 6,* 110-111.

Thomson, G. (1964) Relative humidity: Variation with temperature in a case containing wood. *Stud. Conserv., 9,* 153-169.

Thomson, G. (1977) Stabilisation of RH in exhibition cases: Hygrometric half-time. *Stud. Conserv., 22,* 85-102.

Toishi, K. and Miura, S. (1977) Purification of air with zeolite. *Sci. Conserv., 14,* 1-7.

Toledo, F., Sehn, M., Sousa, M., Brazolin, S. and Hackney, S. (2007) The use of glass boxes to protect modern paintings in warm humid museums. In: *Museum Microclimates: Contributions to the Copenhagen conference, 19-23 November 2007*. Ed. by: Padfield, T. and Borchersen, K. Copenhagen, National Museum of Denmark. pp. 261-266.

van der Doelen, G.A. and Boon, J.J. (2000) Artificial ageing of varnish triterpenoids in solution. *J. Photochem. Photobiol. A: Chem., 134, 45*-57.

Townsend, J.H., Thomas, J., Hackney S. and Lerwill A, (2008) The benefits and risks of anoxic display for colorants, In: *Conservation and Access: Contributions to the 2008 IIC Congress, London. London, IIC.* pp.76-81.

Wadum, J. (1992) De betere klimaatdoos. *Het Mauritshuis Nieuwsbrief, 2*, 8-9.

Wadum, J. (1993) Microclimate-boxes revisited. Talk given at the ICOM-CC meeting of the Working Group on the Care of Works of Art in Transit, August, 1993, Washington, D.C.

Wadum, J. (1998) Microclimate boxes for panel paintings. In: *The structural conservation of panel paintings*. *Proceedings of a symposium at the J. Paul Getty Museum, April 1995.* Ed. by: Dardes, K. and Rothe, A. Los Angeles, Getty Conservation Institute. pp. 497-524.

Wadum, J. (2000) Mikroklimeavitrinen ohne Feuchtigkeitspuffer. *Restauro, 106*, 96-100.

Watts, S., Crombie, D., Jones, S. and Yates, S.A. (2007) Museum showcases: specification and reality, costs and benefits. In: *Museum Microclimates: Contributions to the Copenhagen conference, 19-23 November 2007*. Ed. by: Padfield, T. and Borchersen, K. Copenhagen, National Museum of Denmark. pp. 253-260.

Weintraub, S. (1982) A new silica gel and recommendations. In: *American Institute for Conservation of Historic and Artistic Works. Preprints of papers presented at the 10th Annual Meeting, Milwaukee, Wisconsin 26-30 May, 1982*. Washington, D.C., AIC. pp. 169-173.

Weintraub, S. (2002) Demystifying silica gel. In: *Proceedings of the 30th Annual Meeting of the American Institute for Conservation. Objects Specialty Group Session.* AIC, Washington (Objects Specialty Group Postprints: Vol. 9). pp. 169-194.

West, R.H., Odlyha, M., Pratt, K., and Hutton, S. (2004) Monitoring the environmental degradation of paint dosimeters used to assess risk for fine art paintings by XPS. *Surf. Interface Anal., 36,* 862-865.

Wise, A., Granowski, C. and Gourley, B. (2005) Out of the box: measuring microclimates in Australian-made Solander boxes. In: *Art on paper: mounting and housing*. Ed. by: Rayner, J., Kosek, J.M. and Christensen, B. London, Archetype., pp. 55-58.

Yu, D., Klein, S.A. and Reindl, D.T. (2001) An evaluation of silica gel for humidity control in display cases. *WAAC, 23*.

Zinn, E., Reilly, J.M., Adelstein, P.Z. and Nishimura, D.W. (1994) Air pollution effects on library microforms. In: *Preventive conservation practice, theory and research. Preprints on the contributions to the Ottawa Congress, 12-16 September 1994.* Ed. by: Roy, A. and Smith, P. London, IIC. pp. 195-201.

Appendix 1

Results from the environmental measurements performed in PROPAINT

Table 1-1: Results from the dosimeter measurement in PROPAINT.

			DOSIMETERS RESULTS							
			NILU		*Fraun hofer*	*Birkbeck*				
End-User Location	**Site**	**Frame/ Room (F/R)**	**EWO (abs unit)**	**stdv**	**GSD (abs unit)**	**Lead C. (mg/m2)**	**Lead PQC (% change)**	**stdv**	**R. Mastic (1000*delt a_f/F0)**	**stdv**
1.1 SIT-Artyd workshop (SIT)	Madrid (ES)	F[1]	0.00244	0.0007	1.070	-	-	-	-	-
1.1 SIT-Artyd workshop (SIT)	Madrid (ES)	F[2]	0.00279	0.0013	0.830	52573.00	54.90	0.12	3.98	1
1.1 SIT-Artyd workshop (SIT)	Madrid (ES)	R	0.02039	0.0005	0.010	-	-	-	-	-
1.1 SIT-Artyd workshop (SIT)	Madrid (ES)	R	-	-	-	-	-	-	-	-
1.1 SIT-Artyd workshop (SIT)	Madrid (ES)	F[3]	-	-	-	-	-	-	-	-
1.1 SIT-Artyd workshop (SIT)	Madrid (ES)	F[4]	-	-	-	-	-	-	-	-
1.1 SIT-Artyd workshop (SIT)	Madrid (ES)	F[5]	-	-	-	-	-	-	-	-
2. National Gallery (NG)	Oslo (NO)	F	0.00000	0.0003	0.025	802.47	-	-	-	-
2. National Gallery (NG)	Oslo (NO)	R	0.01776	0.0029	0.013	ND	-	-	-	-
3.1. English Heritage, Apsley House (EH. A.H.)	London (UK)	F	0.00225	0.0032	0.012	58.50	12.13	0.18	5.36	0.90
3.1. English Heritage, Apsley House (EH. A.H.)	London (UK)	R	0.03595	0.0005	0.014	116.96	10.62	0.18	25.4	0.66
3.2. English Heritage, Kenwood (EH. K.)	London (UK)	F	0.00472	0.0067	0.282	1746.03	29.44	0.16	2.2	1
3.2. English Heritage, Kenwood (EH. K.)	London (UK)	R	0.02394	0.0036	0.008	ND	-	-	13	0.83
4.1. Tate Britain (TB)	London (UK)	F	0.00287	0.0013	0.150	1520.47	40.46	0.16	5.81	0.9
4.1. Tate Britain (TB)	London (UK)	R	0.01902	0.0018	0.040	946.50	24.43	0.14	25.5	0.66
4.2. Tate Store (TS)	London (UK)	F	0.00025	0.0010	0.280	3518.52	27.33	0.16	5.36	0.9
4.2. Tate Store (TS)	London (UK)	R	0.00250	0.0015	0.020	1250.00	11.85	0.18	4.72	0.9
5.1. Danish National Gallery (SMK1)	Copenhagen (DK)	F	0.00820	0.0075	0.016	1812.87	-	-	-	-
5.1. Danish National Gallery (SMK1)	Copenhagen (DK)	R	0.02664	0.0005	0.019	ND	-	-	-	-
5.2. Rubens frame in transit (SMK2)	Copenhagen (DK)	F	0.00561	0.0000	0.077	653.59	16.80	0.18	1.83	1
5.3. Rubens frame - empty (SMK)	Copenhagen (DK)	F	0.00091	0.0008	0.128	-	-	-	-	-
5.3. Rubens frame - empty (SMK)	Copenhagen (DK)	R	0.02416	0.0005	0.020	-	-	-	-	-
6.1. Fine Art Museum (MBV)	Valencia (ES)	F	0.02024	0.0009	0.025	492.42	12.55	0.18	10.7	0.83

6.1. Fine Art Museum (MBV)	Valencia (ES)	R	0.04642	0.0078	0.017	ND	3.13	0.20	29.16	0.66
7.1. National Museum of Art (MNA)	Mexico City (MX)	F	0.00257	0.0004	0.018	340.91	10.22	0.18	0.5	1
7.1. National Museum of Art (MNA)	Mexico City (MX)	R	0.03576	0.0007	0.014	ND	4.83	0.22	22.57	0.66
8.1. Germanic National Museum (GNM)	Nürnberg (GE)	F	0.00510	0.0043	0.136	1587.30	-	-	-	-
8.1. Germanic National Museum (GNM)	Nürnberg (GE)	R	0.04850	0.0417	0.014	45.45	-	-	-	-
9.1. National Museum of Krakow (Leonardos frame; NMK1)	Krakow (PO)	F	0.01837	0.0001	0.0630	-	-	-	-	-
9.1. National Museum of Krakow (Leonardos frame; NMK1)	Krakow (PO)	R	0.02548	0.0004	0.0540	-	-	-	-	-
9.2. National Museum of Krakow (new frame; NMK2)	Krakow (PO)	F	0.00169	0.0009	0.0630	2073.37	-	-	-	-
9.2. National Museum of Krakow (new frame; NMK2)	Krakow (PO)	R	0.01780	0.0003	0.0500	273.55	-	-	-	-
10.1. Uffizi Gallery (UG)	Firenze (IT)	F	-	-	-	-	-	-	-	-
10.1. Uffizi Gallery (UG)	Firenze (IT)	R	-	-	-	-	-	-	-	-
11. National Research Institute of Cultural Properties (NRICP)	Tokyo (JP)	R	0.0095	0.0017	-	-	-	-	-	-

[1] With mockpainting and separated dosimeters. [2] With mockpainting and dosimeters together. [3] New empty frame. [4] New empty - "bad" materials. [5] New empty - "good" materials

Table 1-2: Results from the passive diffusion gas sampler measurement in PROPAINT.

			PASSIVE DIFUSSIVE SAMPLERS RESULTS (µg m^{-3})											
End-User Location	**Site**	**Frame/ Room (F/R)**	**TVOC**	**NO2**	**stdv**	**SO2**	**stdv**	**O3**	**stdv**	**Acetic Acid**	**stdv**	**Formic Acid**	**stdv**	**Formaldehyde**
1.1 SIT-Artyd workshop (SIT)	Madrid (ES)	F[1]												
1.1 SIT-Artyd workshop (SIT)	Madrid (ES)	F[2]	28242.23	0.50		0.70		0.50		2534.00	634.00	225.00	37.00	5.80
1.1 SIT-Artyd workshop (SIT)	Madrid (ES)	R		19.20	0.80	1.70	0.00	4.20		186.00	56.00	52.00	4.00	14.80
1.1 SIT-Artyd workshop (SIT)	Madrid (ES)	R	4544.64	20.60	0.60					148.94	11.03	32.42	1.55	
1.1 SIT-Artyd workshop (SIT)	Madrid (ES)	F[3]	3372.48	4.00						604.16	38.97	68.69	8.96	
1.1 SIT-Artyd workshop (SIT)	Madrid (ES)	F[4]	5274.10	11.00						122.53	8.53	37.90	2.28	
1.1 SIT-Artyd workshop (SIT)	Madrid (ES)	F[5]	3650.39	1.00						319.61	82.12	25.80	3.36	
2. National Gallery (NG)	Oslo (NO)	F	1112.65	1.00		0.50		0.50		143.28	50.36	116.22	49.17	1.23
2. National Gallery (NG)	Oslo (NO)	R	39.05	27.50	1.23	0.70	0.06	10.40	2.00	16.29	3.21	12.65	0.55	0.67
3.1. English Heritage, Apsley House (EH. A.H.)	London (UK)	F	163.28	1.00		0.50		5.90		92.33	2.91	12.50	0.00	4.40
3.1. English Heritage, Apsley House (EH. A.H.)	London (UK)	R	176.73	42.50	3.70	1.60	0.06							0.52
3.2. English Heritage, Kenwood (EH. K.)	London (UK)	F	1612.17	2.00		0.50		0.50		1547.97	146.44	510.50	85.96	5.61
3.2. English Heritage, Kenwood (EH. K.)	London (UK)	R	2007.77	20.20	0.70	0.60	0.06	9.00	0.30	52.11	1.22	11.14	0.23	0.69
4.1. Tate Britain (TB)	London (UK)	F	3994.89	2.00		0.50		0.50		542.52	68.81	15.38	1.83	0.83
4.1. Tate Britain (TB)	London (UK)	R	179.97	35.60	0.30	0.60	0.00	3.10	0.60	106.01	0.28	1.88	0.08	2.35
4.2. Tate Store (TS)	London (UK)	F	706.84	1.00		0.50		0.50		1362.10	1.88	135.83	24.42	2.36
4.2. Tate Store (TS)	London (UK)	R		1.20	0.01	0.50	0.17	2.10	0.90	300.50	13.24	2.10	0.08	1.60
5.1. Danish National Gallery (SMK1)	Copenhagen (DK)	F	4346.96	4.00		0.90		0.50		1069.48	197.95	160.74	32.70	UD
5.1. Danish National Gallery (SMK1)	Copenhagen (DK)	R	75.52	13.20	0.30	1.00	0.05	12.70	0.70	43.38	3.40	17.77	3.86	0.60
5.2. Rubens frame in transit (SMK2)	Copenhagen (DK)	F												
5.3. Rubens frame - empty	Copenhagen	F												

(SMK)	(DK)												
5.3. Rubens frame - empty (SMK)	Copenhagen (DK)	R											
6.1. Fine Art Museum (MBV)	Valencia (ES)	F	4692.40	0.00		0.50		2.70		434.48	35.61	155.63	9.00	0.78
6.1. Fine Art Museum (MBV)	Valencia (ES)	R	106.96	26.50	0.20	1.00	0.00	8.10	2.40	46.80	8.06	9.50	0.36	1.42
7.1. National Museum of Art (MNA)	Mexico City (MX)	F	5217.27	0.00		0.30		1.40		519.33	157.98	93.50	19.34	1.05
7.1. National Museum of Art (MNA)	Mexico City (MX)	R	222.95	41.20	1.80	5.50	0.30	19.90	1.10	37.82	9.32	20.66	4.19	0.21
8.1. Germanic National Museum (GNM)	Nürnberg (GE)	F	477.26	1.00		0.90		0.50		1831.10	168.70	136.53	182.93	UD
8.1. Germanic National Museum (GNM)	Nürnberg (GE)	R	654.89	14.50	0.20	0.90	0.09	6.80	0.30	37.24	1.96	12.92	0.34	0.90
9.1. National Museum of Krakow (Leonardos frame; NMK1)	Krakow (PO)	F	107.41	2.00		0.90		3.30		316.98	70.89	0.85	1.10	4.15
9.1. National Museum of Krakow (Leonardos frame; NMK1)	Krakow (PO)	R	60.87	23.00	0.00	1.80	0.10	7.40	0.90	22.84	14.95	10.30	5.47	0.55
9.2. National Museum of Krakow (new frame; NMK2)	Krakow (PO)	F	1156.29	0.00		1.00		0.50		501.74	260.38	10.24	0.51	0.36
9.2. National Museum of Krakow (new frame; NMK2)	Krakow (PO)	R	117.70	10.00	0.00	1.10	0.01	2.00	0.40	175.22	96.81	6.50	0.18	1.41
10.1. Uffizi Gallery (UG)	Firenze (IT)	F		2.17		0.72		<0,1		81.11		51.58		
10.1. Uffizi Gallery (UG)	Firenze (IT)	R		14.40		1.12		2.44		32.60		7.28		
11. National Research Institute of Cultural Properties (NRICP)	Tokyo (JP)	R												

[1] With mockpainting and separated dosimeters. [2] With mockpainting and dosimeters together. [3] New empty frame. [4] New empty - "bad" materials. [5] New empty - good" materials

Table 1-3: Climate results

			Climate				
End-User Location	**Site**	**Frame/Room (F/R)**	**T (ºC)**	**RH (%)**	**UV (mW m^{-2})**	**Light (Lux)**	**Light Dose - 1 Year (Lux hours)**
1.1 SIT-Artyd workshop (SIT)	Madrid (ES)	F[1]	-	-	-	-	-
1.1 SIT-Artyd workshop (SIT)	Madrid (ES)	F[2]	19,37	50,19	-	-	-
1.1 SIT-Artyd workshop (SIT)	Madrid (ES)	R	20,31	48,93	-	-	-
1.1 SIT-Artyd workshop (SIT)	Madrid (ES)	R	-	-	-	-	-
1.1 SIT-Artyd workshop (SIT)	Madrid (ES)	F[3]	-	-	-	-	-
1.1 SIT-Artyd workshop (SIT)	Madrid (ES)	F[4]	-	-	-	-	-
1.1 SIT-Artyd workshop (SIT)	Madrid (ES)	F[5]	-	-	-	-	-
2. National Gallery (NG)	Oslo (NO)	F	-	-	0,00	360,00	725852
2. National Gallery (NG)	Oslo (NO)	R	21,48	24,94	0,40	417,00	1388587
3.1. English Heritage, Apsley House (EH. A.H.)	London (UK)	F	15,75	53,67	-	-	-
3.1. English Heritage, Apsley House (EH. A.H.)	London (UK)	R	18,34	39,24	-	-	-
3.2. English Heritage, Kenwood (EH. K.)	London (UK)	F	15,93	47,24	-	-	-
3.2. English Heritage, Kenwood (EH. K.)	London (UK)	R	-	-	-	-	-
4.1. Tate Britain (TB)	London (UK)	F	15,60	53,00	-	-	-
4.1. Tate Britain (TB)	London (UK)	R	15,55	51,20	-	-	-
4.2. Tate Store (TS)	London (UK)	F	15,17	56,80	-	-	-
4.2. Tate Store (TS)	London (UK)	R	16,00	55,00	-	-	-
5.1. Danish National Gallery (SMK1)	Copenhagen (DK)	F	21,23	53,39	-	-	1303571
5.1. Danish National Gallery (SMK1)	Copenhagen (DK)	R	21,67	39,57	-	-	2105769
5.2. Rubens frame in transit (SMK2)	Copenhagen (DK)	F	-	-	-	-	-
5.3. Rubens frame - empty (SMK)	Copenhagen (DK)	F	21,89	58,51	-	-	-
5.3. Rubens frame - empty (SMK)	Copenhagen	R	-	-	-	-	-

	(DK)						
6.1. Fine Art Museum (MBV)	Valencia (ES)	F	19,66	54,28	-	-	-
6.1. Fine Art Museum (MBV)	Valencia (ES)	R	20,02	48,44	-	-	-
7.1. National Museum of Art (MNA)	Mexico City (MX)	F	-	-	-	-	-
7.1. National Museum of Art (MNA)	Mexico City (MX)	R	20-22	40-45	-	-	-
8.1. Germanic National Museum (GNM)	Nürnberg (GE)	F	-	-	-	-	-
8.1. Germanic National Museum (GNM)	Nürnberg (GE)	R	17,95	44,48	-	-	1330729
9.1. National Museum of Krakow (Leonardos frame; NMK1)	Krakow (PO)	F	16,94	37,88	-	-	-
9.1. National Museum of Krakow (Leonardos frame; NMK1)	Krakow (PO)	R	17,74	37,13	-	-	-
9.2. National Museum of Krakow (new frame; NMK2)	Krakow (PO)	F	16,82	56,96	-	-	-
9.2. National Museum of Krakow (new frame; NMK2)	Krakow (PO)	R	-	-	-	-	-
10.1. Uffizi Gallery (UG)	Firenze (IT)	F	-	-	-	-	1955357
10.1. Uffizi Gallery (UG)	Firenze (IT)	R	-	-	-	-	1955357
11. National Research Institute of Cultural Properties (NRICP)	Tokyo (JP)	R	-	57,50	-	-	-

[1] With mockpainting and separated dosimeters. [2] With mockpainting and dosimeters together. [3] New empty frame. [4] New empty - "bad" materials. [5] New empty - "good" materials

Appendix 2

GC-MS analytical investigations

GC-MS analytical techniques

GC/MS

6890N GC System Gas Chromatograph (Agilent Technologies, Palo Alto, CA, USA) coupled with a 5975 Mass Selective Detector (Agilent Technologies) single quadrupole mass spectrometer equipped with a PTV injector. The mass spectrometer was operated in the EI positive mode (70 eV), transfer line: 280 °C, investigated mass range: 50m/z – 850m/z. The PTV injector was used in splitless mode. Chromatographic separation was performed with a chemically bound HP-5MS fused silica capillary column (Agilent Technologies). The carrier gas was helium (99.995% purity). This instrument was used for the analysis of triterpenoid resins and volatile constituents of MS2A resin.

For the analysis of terpenoid resins the chromatographic oven was programmed as follows: 80°C, isothermal for 2 min, 6°C/min up to 300°C, 300°C isothermal for 30 min; carrier gas flow was kept at the constant value of 1.5ml/min. The PTV injector was kept 320°C
For the analysis of the volatile components of MS2A fraction the chromatographic oven was programmed as follows: 50°C for 2 min, 20°C/min up to 280°C, 280°C for 10 min; carrier gas flow was kept at the constant value of 1.2ml/min. The PTV injector was kept 280°C.

Py/GC/MS

Pyroprobe 5000 (CDS, Analitical). The pyrolyser was used for both thermal desoprtion analysis and pyrolysis of synthetic resins. In all cases transfer line was kept at 300°C and valve oven at 290°C.
The Pyroprobe 5000 parameters for MS2A analyses are as follows:
- thermal desorption at 130°C; probe initial temperature 50°C, final temperature 130°C, speed 20°C/mS; interface 130°C;
- thermal desorption at 250°C; probe initial temperature 50°C, final temperature 250°C, speed 20°C/mS; interface 130°C;
- pyrolysis at 500°C; probe initial temperature 50°C, final temperature 500°C, speed 20°C/mS; interface 130°C;

The Pyroprobe 5000 parameters for Paraloid B72 analyses are as follows:
- thermal desorption 70°C; probe: constant temperature 70°C, interface 70°C;
- pirolisi a 600°C; probe initial temperature 50°C, final temperature 600°C, speed 20°C/mS; interface 130°C;

6890N GC System Gas Chromatograph (Agilent Technologies, Palo Alto, CA, USA) coupled with a 5973 Mass Selective Detector (Agilent Technologies) single quadrupole mass spectrometer equipped with a PTV injector. The mass spectrometer was operated in the EI positive mode (70 eV), transfer line: 280 °C, investigated mass range: 50m/z – 850m/z. The PTV injector was used in split mode at 280°C, split ratio 50:1 for Paraloid B72 and 80:1 for MS2A. Chromatographic separation was performed with a chemically bound HP-5MS fused silica capillary column (Agilent Technologies). The carrier gas was helium (99.995% purity) used at constant flow 1.3 ml/min. The chromatographic oven was programmed as follows: 40°C, isothermal for 5 min, 10°C/min up to 300°C, 300°C isothermal for 10 min.

Analytical Procedures

Triterpenoid resins

Samples in the weight range of 200-450 µg (scraped from the samples by means of a scalps), were subjected to extraction with 1000 µl dichloromethane and 500 µl methanol at 20°C for 30 minutes in ultrasonic bath. 50 µl of the resultant solution was evaporated to dryness under nitrogen stream and subjected to derivatisation with 20µl of N,O-bistrimethylsilyl-trifluoroacetamide (BSTFA), 50µl isooctane (solvent) and 5µl of tridecanoic acid solution at 60°C for 30min. At the end 2 µl were injected into the GC-MS.

MS2A and MS2A+ Tinuvin 292

✓ Analysis of low molecular weight compounds.

Samples were obtained with scissors from the samples: about 1,5 x 5 mm for each analysis. Each sample was extracted in 50 µl of acetone in ultrasonic bath at 60°C for 3 minutes. After removal of the metallic strip, the extracted solution was dried under nitrogen and redissolved in 10 µl of acetone. 2 µl were injected into the GC/MS. To help in the compound identification the raw resin was also subjected to the same derivatisation procedure described for triterpenoids.

✓ Thermal desorption and pyrolysis.

Samples were obtained with scissors from the samples: about 1,5 x 5 mm for each cycle of analyses (thermal desorption at 130°C, thermal desorption at 250°C and pyrolysis at 500°C). Each sample was then inserted into a prepyrolised quartz tube and applied to the top of the probe wire. For each analysis the probe was inserted into the pyrolyser and subjected to thermal desorption at 130°C, thermal desorption at 250°C and pyrolysis at 500°C, remaining in the pyroliser for 3 minutes. Each thermal treatment was assisted by GC/MS runs, according to the conditions described previously.

Paraloid B72

✓ Thermal desorption and pyrolysis.

Samples were obtained with scissors from the varnish samples: about 1,5 x 5 mm for each cycle of analyses (thermal desorption at 70°C, and pyrolysis at 600°C). Each sample was then inserted into a prepyrolised quartz tube and applied to the top of the probe wire. For each analysis the probe was inserted into the pyrolyser and subjected to thermal desorption at 70°C, and pyrolysis at 600°C, remaining in the pyroliser for 3 minutes. Each thermal treatment was assisted by GC/MS runs, according to the conditions described previously.

Dynamic Mechanical Thermal Analysis (DMA)

Dynamic mechanical thermal analysis (DMA) is used extensively in polymer science for characterisation of materials (Turi, 1981). It was first used in conservation science to study the effect of humidification and of solvent cleaning on paint films (Hedley et al., 1990) and primed canvas samples (Foster and Odlyha,1997). In PROPAINT DMA was selected as it measures the glass transition temperature (*Tg*) of polymeric materials, and this gave an indication of the physicochemical state of the varnish. Both the Rheometric Mark 3 and Triton Technology DMA instruments were used to measure the viscoelastic properties of the varnishes. A variable amplitude sinusoidal mechanical stress was applied to the sample to produce a sinusoidal strain of preselected amplitude. Some DMA measurements also were made using the controlled humidity generator which enabled the RH of the sample chamber to be programmed to a selected RH.

In addition spatially resolved measurements were made of the softening temperatures of varnish using micro-thermal analysis. This consisted of an Explorer AFM (Veeco,Santa Barbara<USA) that was modified with a micro-thermal analysis unit (TA Instruments,USA). Experiments were performed with a commercially available Wollaston wire probe(Veeco). This probe was calibrated with onset of melting of selected polymeric materials polycaprolactone Tm=58C,polymethylmethacrylate Tm=150C and polyethylenephthalate Tm=250C.

Samples were cut from the sheets provided (10mms x 15mm) and clamped for measurements in bending mode. Samples were heated at 3ºC/min from 30ºC to 200ºC using a dynamic load at a frequency of 1Hz . The resulting data provided values for tan δ (ratio of inelastic/elastic moduli) with temperature. The maximum in tan delta was taken as the *Tg* of the sample. Measurements in duplicate were made of the six samples in the "as received" state. For the micro-thermal analysis samples were immobilized for the measurements.

Additional thinner resin mastic films on steel were also prepared and measured as changes could be quantified by reflectance FTIR as well as DMA. These thinner films were exposed together with the RM-PQC crystal dosimeters.

MALDI-MS (Matrix Assisted Laser Desorption Ionization-Mass Spectrometry)
MALDI is a "soft" ionization process that produces (quasi)molecular ions from large nonvolatile molecules, such as proteins, oligonucleotides, polysaccharides, and synthetic polymers, with minimum fragmentation. A small molecular weight organic matrix is added to the analyte to overcome molecular photo-dissociation of the sample ions induced by direct laser irradiation. Recent work (Scalarone, 2005) has shown the suitability of MALDI-FOF mass spectrometry for examining highly oxidised terpenoids.

All MALDI spectra were recorded on an Applied Biosystems (Framingham, MA, USA) Voyager TOF mass spectrometer equipped with a nitrogen laser (337 nm). MALDI mass spectra were recorded in the positive-ion mode and were averages of 50 individual laser shots. Spectra were also recorded in triplicate and the average spectrum was used for analysis. The accelerating voltage was set at 20 kV, the focusing guide wire was at 0.01% and the extraction delay time was 250 ns. Spectra were externally calibrated using des-arg-bradykin, angiotensin, glu-fibrinopeptide B and neurotensin standards.

Small strips of varnish on steel were cut and placed into small vials and varnish was extracted using the appropriate solvents (80% aqueous for resin mastic, ethanol for dammar, and toluene for MS2A). One µL of the extract was then mixed with an equal volume of matrix solution (2,5-dihydroxybenzoic acid, 10 mg/mL in 50% ethanol and 0.1% trifluoroacetic acid), and 1 µL aliquots of the mixture spotted on to the MALDI target plate. The samples were allowed to dry in air.

Atomic Force Microscopy

Atomic force microscopy was performed using a Dimensional 3100 – Nanoscope IV AFM (Veeco, Santa Barbara, United States). The instrument was operated in contact mode using cantilever A (cantilever length: 90-119 μm, cantilever width: 14-16 μm, spring constant: 0.08 N/m, resonant frequency: 24-44 kHz). The scan rates were ca. 1 Hz, with scan sizes between 10 and 50 μm. Atomic force microscopy (AFM) facilitates highly accurate measurements of the topographic height (**z** axis of image). All samples were imaged in the contact mode using a DNPS silicon nitride cantilever with a tip radius of ca. 10 nm. The topography and vertical deflection were recorded simultaneously. Varnish strips were immobilized and the surface analysed in the "as received state". Atomic Force Microscopy measurements were also performed using the Nanosurf easyScan2 AFM. This was also used in contact mode. The rationale for using this instrument is that it is portable and possible to transport to conservation science laboratories.

SIMS (Secondary Ion Mass Spectrometry)

SIMS analysis was performed using a Mini-SIMS instrument (Millbrook Scientific Instruments Ltd.) equipped with a 5kV gallium ion source in static SIMS mode.

SIMS is a technique which is used to analyze the composition of solid surfaces by sputtering the surface of the specimen with a focused primary ion beam and collecting and analyzing ejected secondary ions. These secondary ions are measured with a mass spectrometer

Samples were examined in the "as received" state. For B72 some of the samples were washed with n-heptane (Analar grade, Sigma Aldrich). This was necessary since analysis of the 'as received' varnish surfaces indicated that four of the six surfaces were contaminated by silicone (PDMS) species, as characterised by the positive fragment m/z=73+ ($C_2H_5SiO^+$). As a result, it was decided that all the surfaces should be washed in n-heptane which is an excellent solvent for PDMS but would not be expected to dissolve acrylic-based varnishes such as B-72.

References

de la Rie, R., Shedrinsky,A.M., "The Chemistry of Ketone Resins and the Synthesis of a Derivative with Increased Stability and Flexibility " Studies in Conservation, Vol. 34, No. 1 (Feb., 1989), pp. 9-19.

Foster, G., Odlyha,M., and Hackney, S. J. "Evaluation of the Effects of Environmental Conditions and Preventive Conservation Treatment on Painting Canvases", Thermochimica Acta 294, (1997), 81-89.

Hedley, G., Odlyha,M., Burnstock,A., Tillinghast, J and Husband,C "A study of the mechanical and surface properties of oil paint films treated with organic solvents and water", Cleaning, retouching and coatings, International Institute for Conservation, Congress Preprints (1990) 98-105.

Scalarone, D., Duursma,M.C., Boon,J.J., Chiantore,O., "MALDI-TOF mass spectrometry on cellulosic surfaces of fresh and photo-aged di- and triterpenoid varnish resins" Journal of Mass Spectrometry 2005; 40 p. 1527–1535.

Turi, E. A. "Thermal Characterisation of Polymeric Materials", Academic Press, (1981).

Appendix 3

Microclimate frame details

Table 3-1: Microclimate frame characteristics

	Krakow, Leonardo (NMK1)	Krakow, New Frame (NMK2)	Nurnberg (GNM)	EH, Aspley (EH A.H.)	EH, Kenwood (EH K)	Tate, Britain (Tate B)	Tate, Store (Tate S.)	Danish National Gallery (SMK)	SIT	Valencia (SMB)	Oslo (NG)
Type of microclimate frame	Purpose build	Modified classic	Hahn Protector	Modified classic	new frame	Modified classic	Modified classic	Modified classic	SIT new frame	SIT new frame	Modified classic
Age of microclimate frame **(*)**	5	1	6	1	20+	100	15	1	2	3	35-40
Materials inside microclimate frame	glass fiber board tapestry Velcro ®	glass poly-carbonate sheet aluminium profiles aluminium tape	glass Rubber aluminium profiles Tape	glass wood silicone seal aluminium foil oil tempered hardboard brass screws	wood oil tempered hardboard silicone seal aluminium foil PVC coated cable brass screws	softwood glass oil tempered hardboard brass screws Gummed paper PE film Gesso/gold leaf steel screws	softwood glass oil tempered hardboard brass screws PE film Gesso/gold leaf paper clips steel screws	balsa wood acrylic paint felt screws cork aluminium tape glass polycarbonate board	acrylic paint silicon tape metacrilic (plexi) aluminium plate polycarbonate board Artsorb ® stainless steel Neoprene glass	Metacrilic (plexi) glass Silicon tape Poly-carbonate board Artsorb ® Neoprene aluminium plate stainless steel aluminium tape	wood glass poly-carbonate board

*) **at the time of PROPAINT project, c. 2008**

Table 3-2: Microclimate frame inner dimensions.

Enduser/partner	Frame name	Frame (lenght)	Frame (width)	Frame (depth)	Frame inner surface area	Frame volume
		(mm)	(mm)	(mm)	(m^2)	(m^3)
National Museum in Krakow (NMK1)	Leonardo	1500	1400	150	5.0700	0.3150
National Museum in Krakow (NMK2)	New frame	1240	940	65	2.6146	0.0758
Germanic National Museum (GNM)	Hahn Protector	1330	1010	45	2.8972	0.0604
English Heritage (EH A.H.)	Aspley House	515	380	65	0.5078	0.0111 (note 1)
English Heritage (EH K.)	Kenwood	1680	540	50	2.0364	0.0454
Tate (Tate B.)	Britain	560	330	55	0.4675	0.0102
Tate (Tate S)	Store	810	1140	30	1.9638	0.0275 (note 2)
Statens Museum for Kunst (SMK)	Empty frame exhibited	760	1070	30	1.7362	0.0244
SIT	Test frame for Propaint	1030	680	120	1.8112	0.0840
Fine Art Museum of Valencia (MBV)	SIT frame	970	580	100	1.4352	0.0563
National Gallery, Oslo (NG)	Fru Ragnhild Bäckström	n/a	n/a	n/a	n/a	0.0185 (note 3)

Notes:
1: These values are approximations because frame is oval
2: Volume less than l*w*d due to complicated inner structure of frame
3: Only frame volume reported

Table 3-3: Artefact dimensions.

Enduser/partner	Frame name	Artefact (lenght)	Artefact (width)	Artefact (depth)	Artefact surface area	
		(mm)	(mm)	(mm)	(m^2)	
National Museum in Krakow (NMK1)	Leonardo	850	735	57	1.4302	(note 1)
National Museum in Krakow (NMK2)	New frame	1040	765	20	1.6634	
Germanic National Museum (GNM)	Hahn Protector	1266	949	25	2.5134	
English Heritage (EH A.H.)	Aspley House	n/a	n/a	n/a	n/a	(note 2)
English Heritage (EH K.)	Kenwood	1660	520	10	1.7700	
Tate (Tate B.)	Britain	n/a	n/a	n/a	n/a	(note 3)
Tate (Tate S)	Store	n/a	n/a	n/a	n/a	(note 3)
Statens Museum for Kunst (SMK)	Empty frame exhibited	n/a	n/a	n/a	n/a	(note 3)
SIT	Test frame for Propaint	700	500	20	0.7480	
Fine Art Museum of Valencia (MBV)	SIT frame	963	575	45	1.2459	
National Gallery, Oslo (NG)	Fru Ragnhild Bäckström	870	700		1.2180	(note 4)

Notes:

1: Approximation of thickness, averaged between painting and picture frame

2: Painting inside, but frame is very difficult to open, so dimensions are not measured

3: No object

4: Only frame volume reported

Table 3-4: Total frame + artefact. Dimensions.

Enduser/partner	Frame name	Total inner area frame + artefact)	Frame volume net (Frame – artefact)	Artefact/Frame inner area	
		(m^2)	(m^3)	ratio	
National Museum in Krakow (NMK1)	Leonardo	6.5002	0.2794	0.2821	(note 1)
National Museum in Krakow (NMK2)	New frame	4.2780	0.0599	0.6362	
Germanic National Museum (GNM)	Hahn Protector	5.4108	0.0304	0.8676	
English Heritage (EH A.H.)	Aspley House	n/a	n/a	n/a	(note 2)
English Heritage (EH K.)	Kenwood	3.8064	0.0367	0.8692	
Tate (Tate B.)	Britain	0.4675	0.0102	n/a	
Tate (Tate S)	Store	1.9638	0.0275	n/a	
Statens Museum for Kunst (SMK)	Empty frame exhibited	1.7362	0.0244	n/a	
SIT	Test frame for Propaint	2.5592	0.0770	0.4130	
Fine Art Museum of Valencia (MBV)	SIT frame	2.6811	0.0313	0.8681	
Oslo (NG)	Fru Ragnhild Bäckström	1.2180	n/a	n/a	(note 3)

Notes:

1: Approximation of thickness, averaged between painting and picture frame

2: Painting inside, but frame is very difficult to open, so dimensions are not measured

3: Only frame volume reported

Table 3-5: Site characteristics.

	National Museum in Krakow (NMK1)	National Museum in Krakow (NMK2)	Germanic National Museum (GNM)	EH, Aspley (EH A.H.)	EH, Kenwood (EH K.)	Tate, Britain (Tate B.)	Tate, Store (Tate S.)	Statens Museum for Kunst (SMK)	SIT	Fine Art Museum of Valencia (MBV)	National Gallery, Oslo (NG)
Type of room	public gallery	public gallery	Stair case	public gallery	public gallery	Stairwell	Storage	Public gallery	Workshop	Public gallery	Public gallery
Room dimension (m^3)	121	667	?	1440	165	119	2205	4053	133	1200	924
Building materials room	waxed wooden floor emulsion paint tapestry glass (ceiling) lime plaster	wooden ceiling lacquered wooden floor acrylic emulsion paint Gypsum board lime plaster	Stone	silk plaster wooden floor woollen carpet	wooden door plaster wooden floor	brick plaster paint wood	cement emulsion paint steel screens vinyl floor painting/frames	plaster wooden lacqured floors	acrylic paint metal rubber floor	Bricks plaster stone steel glass MDF painted	paint glass ceiling cork
Number of visitor per day	420	120	20	160	?	50	20	<800	?	200-250	400-700
Ventilation	natural	natural, humidifiers	natural	natural	natural	natural	Air conditioning	Air conditioning	n/a	Air conditioning	natural
Windows	none	surrounding	2 (1,10x450m)	6	1	yes	none	2	none	none	ceiling
UV protection from windows	n/a	blinds UV foil	n/a	blinds	UV film blinds	0,02mW/m2		UV-filters			
Lighting	halogens at painting fluorescent ceiling halogen at night	halogens at painting fluorescent ceiling	fluorescent ceiling	?	?	fluorescent	fluorescent	200W halogen natural fluorescent	fluorescent halogen	Halogen fluorescent	fluorescent natural
UV protection from lights	none						UV-filter			UV-filters	
Other comments	transit room		Summer sun in staircase Oil on wooden stretcher	lux levels below 200	breaks in foils lux levels below 200		no UV	300-375 lux	air pollution from paint workshop	Painting just restored	UV: 0,4mW/m2

Table 3-6: Room volume and air exchange.

Enduser/partner	Frame name	Room volume	Room air exchange rate	
		(m^3)	**(h^{-1})**	
National Museum in Krakow (NMK1)	Leonardo	121	5,76	
National Museum in Krakow (NMK2)	New frame	667	n/a	
Germanic National Museum (GNM)	Hahn Protector	n/a	n/a	(Note 1)
English Heritage (EH A.H.)	Aspley House	1440	0.6-1	(Note 2)
English Heritage (EH. K.)	Kenwood	165	n/a	
Tate (Tate B.)	Britain	119	n/a	
Tate (Tate S.)	Store	2205	n/a	
Statens Museum for Kunst (SMK)	Empty frame exhibited	4053	~ 2	
SIT	Test frame for Propaint	133	n/a	
Fine Art Museum of Valencia (MBV)	SIT frame	1200	n/a	
National Gallery, Oslo (NG)	Fru Ragnhild Bäckström	n/a	n/a	

Notes:

1: Not available, complicated structure, open stairway

2: In daytime, not known for night-time

Appendix 4

Case study in the Mauritshuis museum

EVAPORATION OF FATTY ACIDS AND FORMATION OF WHITISH DEPOSITS ON THE INSIDE OF THE GLASS/ MICROCLIMATE BOXES: A CASE STUDY IN THE MAURITSHUIS

Petria Noble, Head of Paintings Conservation (Noble.P@mauritshuis.nl)
Annelies van Loon, Research Scientist (Van Loon.A@mauritshuis.nl)

Abstract- This article presents a case study regarding the analyses of white deposits that formed on the inside of the glass of the microclimate box in which Gerrit Dou, *The Young Mother*, 1658 (Mauritshuis inv no 32), was housed. Deposits corresponding to dark reddish brown and black areas of the painting were seen to form over a period of a few months, from March to July 2007, when the picture was hanging on an exterior, southwest facing wall. FTIR and EDX analyses (ICN, Amsterdam) revealed that the deposits consist of sodium soaps, most likely in the form of sodium palmitate and stearate. Precise monitoring of the climate conditions carried out in the gallery by Technical University of Eindhoven (2004-2006) demonstrated temperature fluctuations on this wall as high as 31˚C with a corresponding variation in relative humidity from 31-80%. It is hypothesised that a temperature gradient developed inside the microclimate box as a result of contact with the warmed wall and/or exposure to direct sunlight, causing free fatty acids to evaporate out of the paint. The deposition of fatty acids on the inside of the glass is considered to undergo a subsequent reaction with the sodium in the glass to form sodium soaps. The results correspond with earlier published studies regarding ghost-or transferred images on the inside of glass and fatty acid deposits found on the surface of paintings.

Introduction

Paintings in the Mauritshuis are routinely glazed with protective glass to prevent damage from vandalism and accidental damage. Since the early 1990s, panels that are deemed fit to travel, are also regularly sealed in specially adapted frames to minimize climate fluctuations - so called microclimate boxes. The microclimate box currently in use in the Mauritshuis was developed in the early 1990s by Jørgen Wadum (Wadum et al. 1994; Wadum 1995). The microclimate box is produced in house by the framing technician, and is constructed within the existing frame, in which safety glass[4] is held in place on the inside of the frame rebate with aluminium tape, and sealed with a transparent polycarbonate (*Lexan*) backboard, which is also sealed with aluminium tape. If the rebate is not deep enough to accommodate the glass, balsa wood spacer, felt and painting, it is necessary to extend the rebate with a build-up on the

[4] A thickness of 4 mm *Schott Mirogard Protect* safety glass is used in the Mauritshuis for microclimate boxes. *Mirogard Protect* is made of two sheets of low iron float glass with anti-reflective coating on one surface, laminated with a special UV-absorbing interlayer. For data see: http://www.schott.com/architecture/english/download/datenblatt_mirogard_englisch.pdf?PHPSESSID=jte2a46jcn51f6qjen5gvmbf16

reverse of the frame (fig. 1). No sorbent material is added; the buffering role of the panel is considered sufficient. Acclimatisation of the painting in the correct relative humidity is critical for the conditions in the microclimate box.

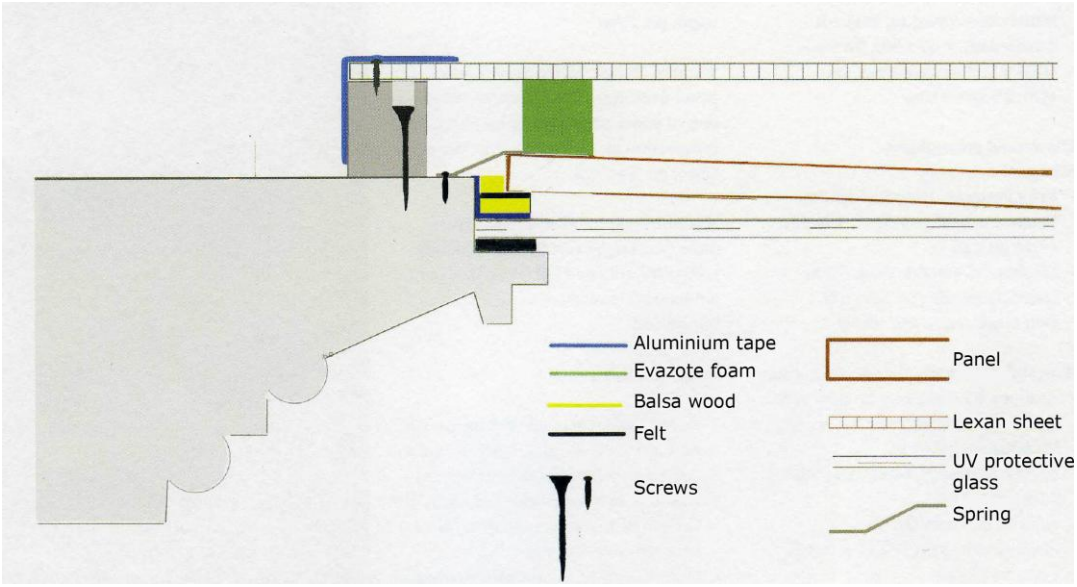


Fig. 1. Diagram showing cross-section of the construction of microclimate boxes used in the Mauritshuis.

Over the course of many years it has been observed by conservators in the Mauritshuis that hazy deposits regularly form on the inside of the glass. This has also been observed in other museums which glaze their paintings. These hazy deposits, often referred to as *ghost-transferred-* or *mirror* images, are disturbing and can severely obscure the art work. Often these deposits are associated with the image, hence the term *mirror* images (Williams 1988; Skaliks 1999). The hazy deposits are greasy in nature and depending on thickness, are greyish or whitish in appearance. In the Mauritshuis they are removed periodically by the framing technician, first with water and green soap[5] using a micro-fibre cloth, followed by wiping with ethanol and damp paper. Concern has developed as to the recurring nature of the deposits and the long term effect on paintings. The reoccurrence of deposits has implications for the microclimate box design and climate conditions in certain locations in the museum. Regular removal of the deposits has furthermore significantly increased the work load for the technical staff: since 2001, when cleaning of the glass began being recorded, hazy deposits on more than 200 paintings have been removed.

Monitoring of climate conditions in the Mauritshuis

During the last renovation of the museum in 1984-86 the museum was equipped with a modern air conditioning system. Between 2004 and 2006 the Mauritshuis along with several other museums participated in a research project - *Project Klimaat Onderzoek Rijksmusea* - initiated by the Erfgoedinspectie. As part of this project the University of Eindhoven (TU/e) was commissioned to monitor the climate conditions in a number of museums including the Mauritshuis (Baan and Duijnhoven, 2005; Marten, Schellen, van Schijndel, Van Aarle, 2007). The various museums were chosen because of their inherently different building type,

[5] Green soap is a weak soap used for household cleaning with a green colour made with plant oil and potassium hydroxide (instead of sodium hydroxide, as is the case for hard soaps). http://nl.wikipedia.org/wiki/Groene_zeep

collection and type of climate installation. For the Mauritshuis, the combination of a monumental historic building with a relatively modern climate installation was considered a valuable case study. The final results of this research were published in 2007 (Meul, V.L.B.M. 2007).

In the Mauritshuis, the exhibition galleries are located on the ground and first floors. Exterior walls in each of the corner galleries contains concealed windows which consist of single-glazed windows closed off with an infrared-absorbing screen and a sheet of *Lexan*. In the galleries these windows are concealed behind fabric-covered, fire retardant 10 mm construction sheeting. Fig. 2 shows the locations of the concealed windows in the first floor galleries. Despite the uniformly conditioned air supplied to each floor of the museum, measurements recorded by TU/e demonstrated strongly varying temperatures and relative humidity in several of the galleries, depending on their orientation with respect to the sun. Galleries facing southwest were shown to have more variation in temperature compared to the galleries facing northeast.[6]

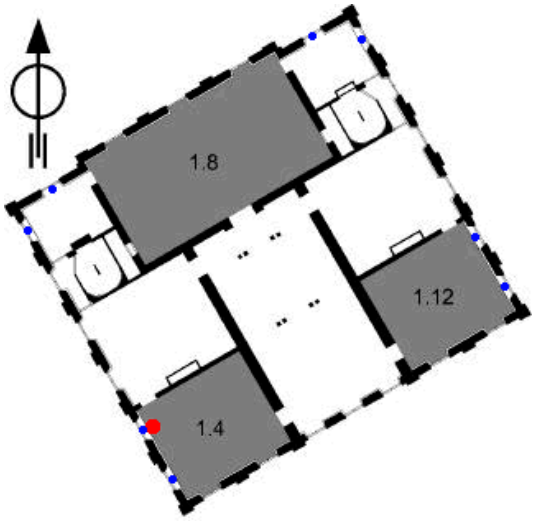


Fig. 2. Floor plan of first floor galleries in the Mauritshuis (from Baan and Duijnhoven 2005). The concealed windows are marked in blue. The location of Dou's, *The Young Mother* between February and July 2007 in the early Rembrandt gallery (1.4), is marked by the red dot.

Case study in The Mauritshuis

Gerrit Dou, *The Young Mother* (MH inv no 32)
Oil on panel
Signed and dated: *GDOV 1658*
73.5 x 55.5 cm

[6] Marten, Schellen, van Schijndel, Van Aarle 2007, pp. 69-111. For cross-section of the construction of the concealed windows, see fig. 5.12 p. 75.

Fig. 3. Gerrit Dou, *The Young Mother*, 1658, panel, MH inv no 32

Physical build-up of the painting

Gerrits Dou's *The Young Mother*, which is painted on a radially cut, single oak plank retains its original thickness and format. The painting appears to have a chalk and lead white ground possibly with the addition of a little umber or black. It has been noted that in some cross-sections the ground now has a brown appearance, which may point to saponification of the lead white particles. In the X-ray, the ground is faintly visible and appears to have been applied with horizontal strokes. Paint cross-sections studied by Groen and Struick van der Loeff demonstrate a multiple layer build-up of numerous thin paint layers. As many as twelve layers of alternating brown and black layers were found in some paint cross-sections.[7] In their study of the dark background paint (using EDX) they identified a high proportion of chalk, along with umber, red ochre, bone black and a little lead white. Wrinkling and wide drying cracks, which are very pronounced in the upper part of the painting are often encountered in Dou's dark paint layers, and clearly point to drying problems. This can be explained by the use of multiple oil-rich layers that contain poor-drying pigments, such as asphalt and carbon/ bone black, possibly in combination with slow-drying walnut oil.[8] In Languri's research into the effect of some of these organic black and brown pigments on the drying of oil, asphalt was

[7] Struick van der Loeff and Groen 1993, p. 101-102.

[8] Struick van der Loeff and Groen 1993, note 14 p.103. In 1986 Raymond White, National Gallery, London using gas chromatography identified asphaltic material in the binding medium of *The Young Mother* by the presence of hopane-like triterpines. In Dou's *Lady at her Toilet*, 1667 (Museum Boijmans van Beuningen) the the presence of phenol suggests the use of Kassel earth in the dark paint layers. See Boersma 2000, pp. 59- 60 and note 24 p. 63.

found to retard the drying process, whereas (pure) Kassel earth (a lignitic pigment) is expected to exert a siccative effect (Languri 2004).

Treatment history

Dou's *The Young Mother* which was bought from the artist's studio for the English Royal Collection and shipped to England in 1660. It was later brought back from England by Stadholder, Willem III to his palace, *Het Loo*. The picture's restoration history dates to 1815 when an inventory was made of the Stadholder's collection after its return from 20-years stay in Paris. Since that date the painting has undergone some 18 documented treatments. The first documented restoration occurred in1816. In the late 19th century the varnish on the picture is recorded as being 'restored' or regenerated numerous times; from the documents treatment most likely also included the use of copaiba balsam. Later the painting underwent four complete restorations: in 1907, 1922, 1954 and 1987. The picture is recorded as being glazed as early as 1907. It also appears to have a history of blistering: first mentioned in 1887, later in 1970, and again in 1986, at which time, prior to restoration a year later, the blisters were laid down with *Mowiol 4-88*, a polyvinyl alcohol adhesive (Struick van der Loeff and Groen 1993). The painting was placed in a modern microclimate box in 1994. The painting was last varnished with dammar during the restoration of 1987.[9]

White deposits on the inside of the glass

- Observations

Between March and July 2007 *The Young Mother* hung on the southwest facing wall in the early *Rembrandt gallery* (now Gallery 9) to the right of Rembrandt's *The Anatomy Lesson of Dr Nicolaes Tulp*, as a pendant to Rembrandt's *Simeon's Song of Praise*, which at that time was hanging to the left of the *Anatomy Lesson*. Hazy deposits were seen to form on the inside of the glass of the microclimate box housing the Dou painting over a remarkably short period of time, between March and July 2007. The deposits were first seen on 14 March 2007 during a routine 'gallery check' and were subsequently documented with photography in the galleries (Rachel Morrison, 4 April 2007). It was noted that the heaviest deposits correspond to dark reddish brown and black areas, in the upper part of the painting. Thereafter the painting continued to be monitored. In July 2007 it was decided to remove the picture from the wall, open the microclimate box, document and take samples of the deposits, clean the inside of glass and reframe the painting. When the glass was removed it could be seen that thin greyish vertical smears were concentrated in the bottom 2/3 of the glass. In the upper portion of the glass the deposits were thicker. Here, long oval-shaped deposits measuring 5 x 1 cm were concentrated forming an arch shape roughly corresponding with the shape of the panel. A number of thicker deposits were also visible in the centre of the glass towards the bottom edge (figs. 4 and 5). When the painting was unframed the surface of upper portions of the painting also appeared to be covered in fine whitish deposits appearing as a haze.

The painting was then reframed, but not sealed, and hung on an interior wall of the same gallery. Since then no new deposits have been observed. Over the course of the past years similar deposits have been observed to form on the inside of the glass of several other paintings whilst hanging on the same wall.

[9] Conservation report, 'G. Dou, « De Jonge Moeder », 1658', Luuk Struick van der Loeff, 1996, Conservation studio, Mauritshuis.

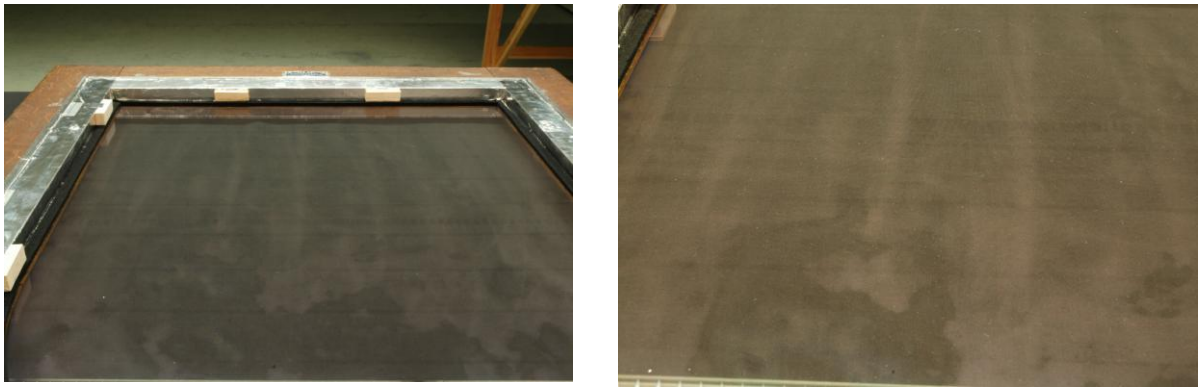


Fig. 4. Whitish deposits on inside of glass of the microclimate box, photographed (on a black cloth), 11 July 2007.

Fig. 5. Detail upper left of *The Young Mother* showing whitish deposits on inside of glass, photographed in the galleries on 14 April 2007. The thicker areas are circled. The deposits formed over a period of a few months while painting was sealed in a microclimate box hanging on the exterior southwest wall of the museum.

Samples

In order to identify the nature of the whitish deposits the following samples were sent to the Dutch Institute for Cultural Heritage (ICN) for analyses.
Sample 1: scraping of whitish deposit, upper left on inside of glass (seen from the front)
Sample 2: extraction with absolute ethanol, same location as sample 1
Sample 3: extraction with xylene, below on inside of glass
Sample 4: extraction with ethanol, same location as sample 1
Samples were removed on 11 July 2007 using a clean scalpel/washed cotton and transferred to glass vials. It was noted that the deposits were not completely soluble in ethanol or xylene.[10]

Results

Identification of the hazy deposits (sample 1) was carried out using Energy dispersive X-ray microanalyses (EDX) and Infrared spectroscopy (FTIR) by the Dutch Institute for Cultural

[10] P. Noble, in Research Proposal submitted to ICN, dated 24 July 2007.

Heritage (ICN). Only sodium (Na) was detected with elemental analysis (fig. 6). With FTIR (in transmittance mode) absorption bands at *c.*1420, 1444 and 1560 cm^{-1} characteristic of the metal (sodium) carboxylate group, and at *c.*2850 and 2915 cm^{-1} attributable to the C-H group of the aliphatic hydrocarbon chain were characterized. This corresponds with absorption bands in the reference spectrum of sodium stearate available (fig. 7). From this it was concluded that the deposits consists of a sodium carboxylate or a mixture of sodium carboxylates (such as sodium palmitate and stearate).[11] The sodium is considered to originate from the glass and appears to have reacted with the saturated fatty acids deposited on the glass to form a mixture of sodium carboxylates (soaps). That the deposits consist of palmitate and stearate clearly indicates an origin from the oil binding medium of the paint. Following the findings of Schilling et al. 1999 one would also expect to find a higher proportion of sodium palmitate in the deposits.

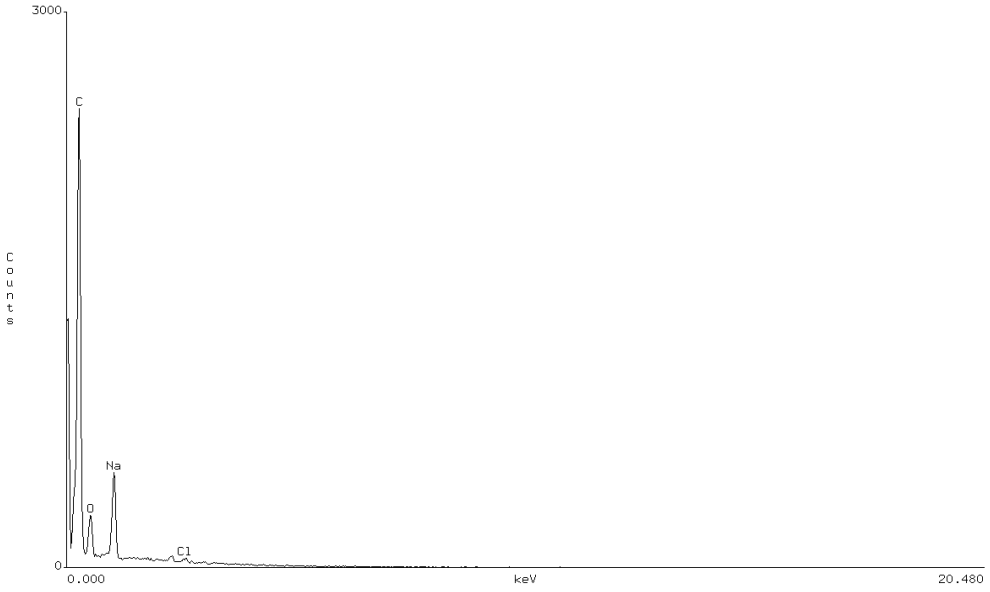


Fig. 6. EDX spectrum of hazy deposit (sample 1). Ineke Joosten, ICN, July 2007.

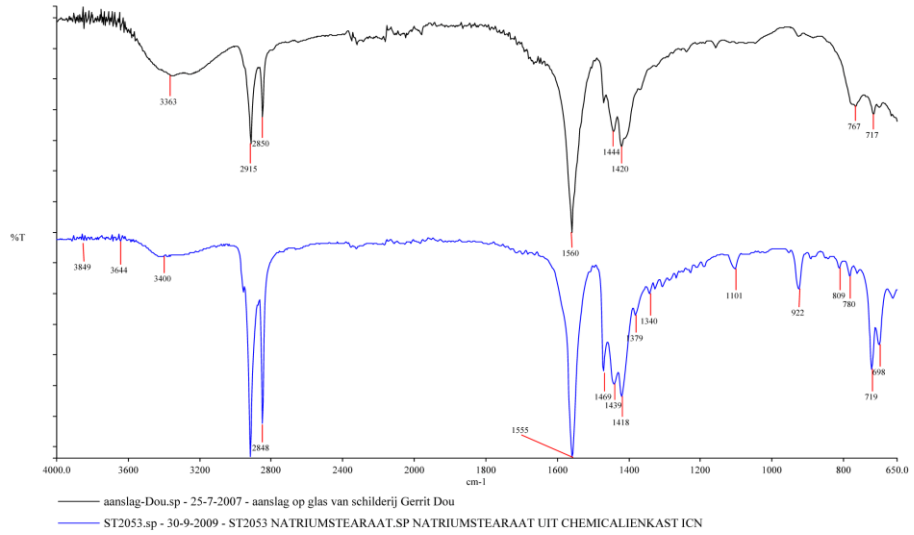
[11] A. Brokerhof, Senior scientist, Research Department, ICN, Amsterdam, in an e-mail dated 27 July 2007.

FTIR onderzoek naar aanslag op binnenkant van het glas van microklimaatdoos van schilderij Gerard Dou

instituut collectie nederland

Object:	glas van microklimaatdoos van schilderij Gerard Dou (Mauritshuis)	Monsternummer:	aanslag-dou
Monsterplaats:	aanslag op glas	Werknummer:	
Reden monstername:	samenstelling	Objectnummer:	
Datum monstername:		Doc. map:	
Uitgevoerd door:	Suzan de Groot	Filenaam FTIR:	aanslag-dou.sp
Apparatuur:	Perkin Elmer Spectrum 100	Filenaam Word:	aanslag-dou.doc
Aantal scans:	40	Analysedatum:	25-7-2007
Methode:	Golden Gate Single Reflection Diamond ATR		

Spectrum



Resultaat:

Het spectrum van de aanslag op het glas vertoont absorptiebanden die overeenkomen met absorptiebanden in het referentiespectrum van natriumstearaat (een natriumcarboxylaat).
Specifieke absorptiebanden in het referentiespectrum van natriumstearaat zijn: 1555 – 1469 – 1439 – 1418 – 719 - 698 cm^{-1}

Conclusie:

De aanslag op het glas bestaat uit een natriumcarboxylaat of een mengsel van verschillende natriumcarboxylaten (zoals natriumstearaat of natriumpalmitaat).

Fig. 7. Above: FTIR spectrum of hazy deposit (sample 1). Below (in blue): FTIR reference spectrum of sodium stearate. Suzan de Groot, ICN, 25 July 2007.

Climate conditions in the early Rembrandt gallery

Measurements of the climate conditions on the southwest-facing wall in the early Rembrandt gallery was carried out by TU/e between 20 October 2004 and 8 February 2006 as part of the *Klimaat Onderzoek Rijksmusea* as described previously. A logger was placed on the wall behind Rembrandt's *The Anatomy Lesson Lesson of Dr Nicolaes Tulp* close to the concealed window where Dou's, *The Young Mother*, a year later would come to hang (for location of the painting see Fig. 2). The temperature on the wall was found to vary between 15.8˚C and 30.5˚C, with a corresponding variation in relative humidity of 31-80%. Fluctuations in temperature and relative humidity per day were found to far exceed accepted guidelines

(greatest in the summer and spring).[12] Fig. 8 illustrates temperature and relative humidity fluctuations of the first floor galleries over a 24 hr period in the winter and the spring.

The fluctuations in climate conditions on and nearby the exterior wall in the early Rembrandt gallery were shown to be the result of two external factors: the poorly insulated exterior wall with concealed window and periodic exposure to direct sunlight coming through partially open south-facing windows.

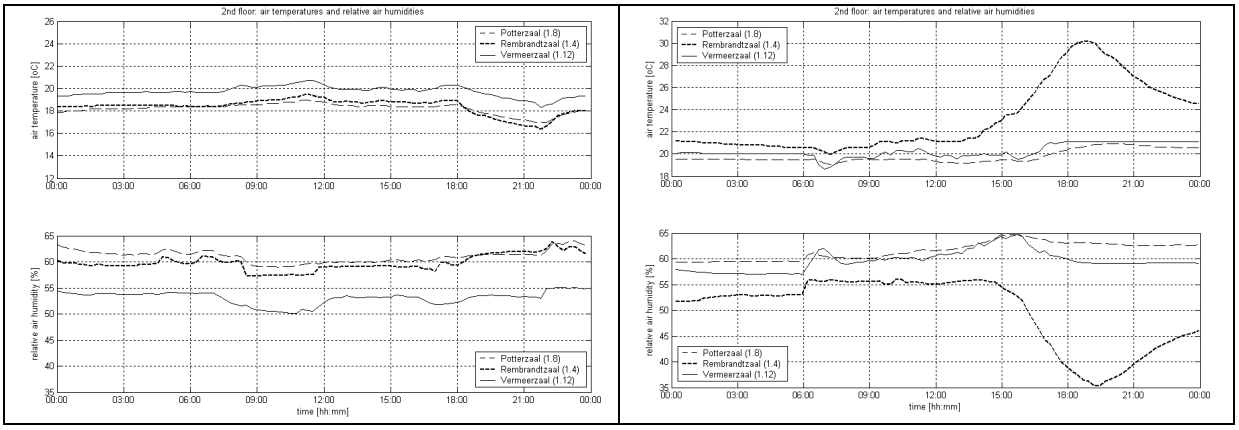


Fig. 8. Temperature and relative humidity measurements from the first floor galleries over a 24 hour period. Left: in the winter, 1 March 2005 and right: in the spring, 27 May 2005 (from Baan and Van Duijnhoven 2005, p. 49).

Measurements on microclimate boxes

Measurements were also carried out by TU/e to test the effectiveness of a microclimate box in extreme conditions: whilst hanging on a cold wall and exposed to direct sunlight (for design of the microclimate box, see Fig. 1). Results clearly demonstrated the positive effect of the microclimate box for maintaining a stable relative humidity so long that the painting was properly acclimatised prior to sealing of the microclimate box. Test paintings were also hung at an angle whereby only the bottom edge made contact with the wall. Accordingly the temperature was found to be colder in the bottom of the box than in the top of the box. For a test painting in a microclimate box exposed to direct sunlight a surface temperature of 31˚C was recorded despite the fact that the sun screens on the windows in the gallery were lowered. The warming of the painting led to a dramatic increase in relative humidity (10%) in the microclimate box, as moisture was given off by the painting in order to reach equilibrium with the warm air on the surface of the painting (fig. 9).[13] In these conditions a temperature gradient is considered to form in the microclimate box between the warm painting and the cooler backboard. Boon et al. (1997) has described the mobility of fatty acids and metal soaps in oil paint as being largely driven by gradients in temperature and moisture.[14]

[12] Marten, Schellen, van Schijndel, Van Aarle 2007, pp. 88.
[13] Baan and Van Duijnhoven 2005, p. 50-51 and Marten, Schellen, van Schijndel, Van Aarle 2007, pp. 97, 101-103, 107, 109.
[14] Boon et al. 2007, p. 21.

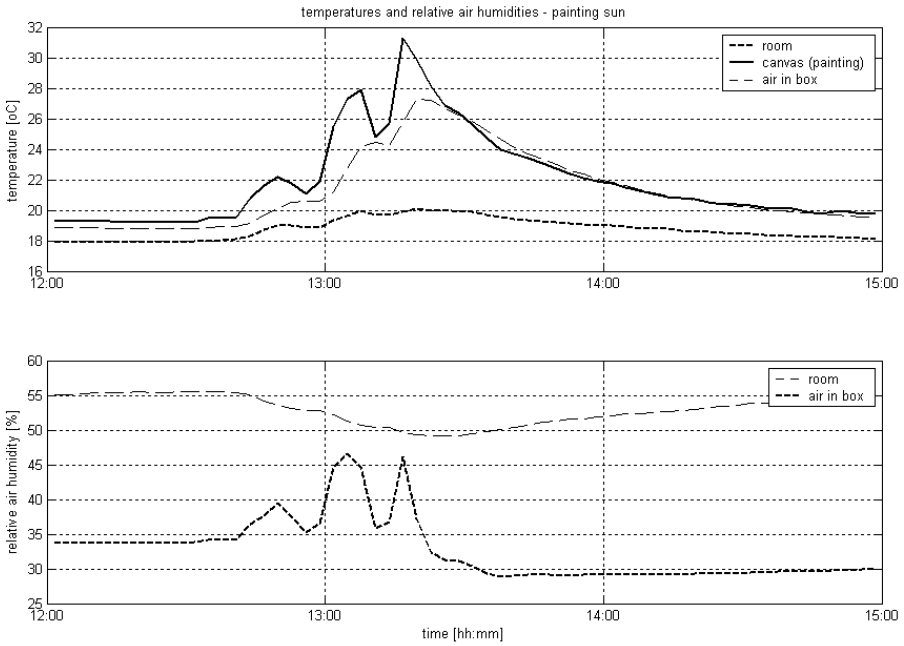


Fig. 9. Temperature and relative humidity measurements from a test painting in microclimate box exposed to direct sunlight, 22 January 2005. (The anomalous low relative humidity of the air in the box (35%) in the lower spectrum was due to insufficient conditioning of the test painting prior to placement in the microclimate box (from Baan and Van Duijnhoven 2005, p. 51)).

Previous studies

- Composition and analysis of ghost- and transferred images

The results of the three earlier published studies regarding the formation of ghost- or transferred images on the inside of the glass of glazed paintings correspond to what has been found in Dou's *The Young Mother*. Using FTIR and Differential Scanning Colorimetry (DSC) as well as hot stage microscopy, Williams identified sodium palmitate in addition to fatty acids and ketones (Williams 1988). In the study by Skaliks, primarily water-soluble sodium soaps and minor amounts of fatty acids were detected using FTIR and GC-MS (Skaliks 1999). Several tentative explanations have been put forward to explain the formation of deposits of free fatty acids and its soaps on the inside of the glass. Williams postulated that the ketones first evaporate from the paint and condense on the glass, after which they oxidise to form carboxylic acids that then undergo reaction with the sodium in the glass. However, in a more recent study using thermogravimetry and gas chromatography of test samples, Schilling et al. showed that free fatty acids readily evaporate to form ghost images, even at room temperature. They also found that palmitic acid evaporates four times faster than stearic acid and twice as fast as azelaic acid which explains the enrichment of palmitate and palmitic acid in the images (Schilling et al. 1999).

- Fatty acid surface deposits

The phenomenon of ghost- or transferred images is related to the deposition of fatty acids on paint surfaces that have been described in the numerous studies of unvarnished modern paintings (Williams 1988; Koller and Burmester 1990; Burnstock et al. 1993; Singer et al. 1995; Ordonez and Twilley 1997; Skaliks 1999; Van den Berg 2002; Keune et al. 2007). In analyses of the deposits, free, saturated fatty acids (palmitic, stearic and azelaic acids) or

related components such as fatty acid salts (lead palmitate and stearate) and paraffinic hydrocarbon (waxy) substances have been identified. This phenomenon has also been shown to occur in Old Master paintings (Van Loon 2008). The fatty acid components are released from the oil matrix through hydrolysis of the glyceride ester link and oxidation reactions at double bonds-, migrate through the paint and deposit on the surface. In addition to transferred images on the inside of the glass, often whitish deposits are also present on the surface of the painting. This also seems to be the case with Dou's *The Young Mother*.

- Influence of the paint composition on the formation of ghost- and transferred images
Analyses of the paint layers that generate transferred images on glass suggest the strong influence of certain binding media, pigments and painting techniques (Williams 1988; Schilling et al. 1999, Skaliks 1999). It has been consistently noted that ghost- or transferred images are more pronounced over certain dark colours, particularly pigments such as black carbonized products, Kassel earth, ochres, ultramarine, vermilion and alizarin, pigments which retard the drying of the oil and, in addition, are highly oil-absorbing. Also this group of pigments lack coordinating metals to interact with the carboxylic acid groups of the oil. It is also significant that the transferred images have not been seen to correspond to white or light coloured passages where pigments that promote cross linking and form more stable oil networks were used. Recent study of a set of artificially aged samples by Keune et al. has shown that for example, lead white and malachite undergo a low degree of hydrolysis, whereas pigments such as vine black, vermilion, red lake, Kassel earth, and red ochre show a high degree of hydrolysis and consequently produce many mono- and di-acids, in free or metal-bound form (Keune et al. 2008).

It is further thought that the porous structure of these dark paint films promotes the migration and evaporation of fatty acids through interparticle passages and connected pores.[15] Like the formation of fatty bloom on chocolate, here moisture and temperature gradients appear to be the driving force. In addition to the fact that dark paints are richer in free fatty acids, dark paints heat up more easily by exposure to heat. Skaliks gives a temperature difference of 4.5˚C between white and dark areas in a painting in freely circulating air. This effect is even stronger when paintings are glazed or enclosed in a microclimate box. With glazed objects this can be as much as 7˚C.[16]

[15] Skaliks 1999. Van Loon 2008, pp.188-191, also note 68.
[16] Skaliks 1999, p. 148.

Discussion

That free fatty acids readily evaporate out of the paint and play an important role in the formation of ghost- or transferred images is clear from the study by Schilling et al. The enrichment of the deposits in palmitic acids can be explained by their shorter hydrocarbon chains and lower boiling point. Fatty acids condense on the glass because the glass is cooler than the paint surface.[17] In *The Young Mother* the saturated monocarboxylic and dicarboxylic acids that formed on the inside of the glass then attached to/ reacted with the sodium out the glass to form sodium carboxylates /palmitate and stearate. It is significant that the heaviest deposits in *The Young Mother* correspond to dark reddish brown and black areas, rich in chalk, bone black and earth pigments since this corresponds with earlier findings that oil-rich paints made with pigments that promote hydrolysis, rather than cross-linking, seem to be particularly susceptible to the formation of fatty acid deposits (Koller and Burmester 1990; Schilling et al. 1999; Skaliks 1999; Boon et al. 2007; Keune et al. 2008). In *The Young Mother*, wrinkling and wide drying cracks visible in the background paint clearly point to problems in drying of the paint. The multiple layers of oil-rich paint shown to contain a high proportion of chalk, umber, bone black and earth pigments not only accounts for the wrinkling defects visible on the paint surface, but would also provide a rich source of free fatty acids.

The location of the painting on the exterior (southwest-facing) wall in the early Rembrandt gallery is also extremely problematic: not only was the painting exposed to fluctuating temperatures and relative humidities as a result of the poorly insulated exterior southwest wall but it also periodically received direct sunlight from the partially open south-facing windows. Skaliks also warns of the effect of exposure to high temperatures through increased light levels.[18] As a result it is hypothesised that a temperature gradient developed inside the microclimate box between the warmed painting and the cooler backboard that resulted in the mobilisation of fatty acids. Here moisture and temperature gradients appear to be the driving force.

The design of microclimate box is also important. In the previous study by Skaliks it was found that the distance between the glass and the paint surface is an important factor that influences the rate at which transferred images are formed. In the internal study carried out between 1986 and 1993 by the Niedersächsischen Landesmuseum Hannover of some 130 glazed objects in relation to transferred images, it was found that the distance between the glass and the painting should be greater than 6 mm, even with small formats. A larger space was shown to have a positive effect on the formation of transferred images due to the (slightly) larger air volume in the microclimate box that takes longer to warm up.[19]

From the research carried out by TU/e it is clear that the use of microclimate boxes exerts a positive influence with regard to maintaining stable relative humidity as long as exposure to increased temperature is avoided.

[17] Skaliks 1999, p. 148.
[18] Skaliks 1993, p. 165.
[19] Skaliks 1999, p. 165.

It is unclear to what extent past treatment plays a role in the formation of transferred images; in the case of *The Young Mother* the painting was last cleaned and varnished in 1987, more than 30 years ago. It is likely that the possible use of copaiba balsam, along with the numerous regenerations of the varnish (with turpentine)[20] that took place in the 19th century, along with the solvent cleanings may have mobilised the free fatty acids in the paint layers making the painting more vulnerable. Over the long term, the regular exudation of free fatty acids from the paint film would be expected to make the oil paint increasingly brittle.

Conclusion

Analyses of whitish deposits on the inside of the glass of a microclimate box on Gerrits Dou, *The Young Mother* (MH inv. nr. 32) was found to consist of a sodium carboxylate, or a mixture of sodium carboxylates, such as sodium palmitate and sodium stearate. These results correspond with earlier published studies regarding the formation of ghost- or transferred images on the inside of the glass of glazed paintings and the formation of fatty acids on the surface of paintings. The deposits, which correspond to dark areas in the painting, were seen to form over a period of a few months as a result of fluctuations in temperature and relative humidity from contact with a poorly insulated exterior wall containing a concealed window. Periodic exposure to direct sunlight is also considered to have played a role. It is hypothesised that a temperature gradient developed inside the microclimate box as a result of warming up, causing free fatty acids to rapidly evaporate out of the paint and condense on the inside of the cooler glass. The saturated fatty acids that formed subsequently underwent a reaction with the sodium in the glass to form sodium soaps.

It is clear that glazed paintings/ paintings in a microclimate box should not be subjected to elevated temperatures. It is therefore important that climate conditions be carefully regulated. More precise and specific monitoring of temperature and relative humidity can moreover reveal problem areas, especially in historic buildings that function as museums. It is important to be aware that sensors may be located in non-representative areas of the galleries that may not reflect real conditions. Temperature and relative humidity readouts from climate systems may also be averaged data, which can be very different from the actual readings where art works are displayed. Independent monitoring in these cases is therefore recommended.

In the Mauritshuis a strict shutter regime is now in place whereby the south-facing windows are closed for most of the day in order to prevent exposure of paintings to direct sunlight. It is recommended that all paintings hanging on exterior walls to be placed in microclimate boxes, with an open air space of at least 2 cm (more depending on size of the painting) between the backboard and the wall to provide sufficient air circulation in order to keep the temperature within the microclimate box as stable as possible. A space of at least 6 mm between the glass and the painting surface will also be incorporated into the modified microclimate box design. The outside of the concealed windows on the southwest façade have now also been fitted with an additional infrared-absorbing film. Close monitoring of the temperature and relative humidity on the southwest-facing exterior wall is being carried out by the Technical Services in collaboration with the Conservation studio. Renovation of the monumental building, with particular attention to the exterior walls is pending.

[20] Washing (*afwassen*) of paintings with turpentine (or green soap) was frequently carried out by the restorer Nicolas Hopman on paintings in the Mauritshuis in the 19th century.

Acknowledgements

The authors are grateful to the Dutch Cultural Institute (ICN), in particular Agnes Brokerhof, Suzan de Groot and Ineke Joosten, for facilitating and carrying out FTIR and EDX analyses of the deposits. We would also like to thank Marco Martens from the Technical University of Eindhoven (TU/e) for his enthusiastic support and fruitful discussions regarding the climate conditions in the Mauritshuis over the past two years. The information regarding the measurements of the climate in the Mauritshuis is based on the report by the *Erfgoedinspectie* (Meul 2007/Marten, Schellen, van Schijndel, Van Aarle 2007).

Bibliography

- Microclimate boxes
Wadum, J., Hummelen, I. J., Kragt, W., Jütte, B. A. H. G. and Sozzani, L., 1994, 'Research Programme Microclimates: Paintings on Panel and canvas'. Poster presented at IIC Ottawa Congress, 12-16 September 1994.

Wadum, J., 1995, 'Microclimate Boxes for Panel Paintings', in *Proceedings of a symposium at the J. Paul Getty Museum, Los Angeles 1995, The Structural Conservation of Panel Paintings*, 497- 524.

- Museum climate
Meul, V.L.B.M., 2007, *Luchtspiegelingen, De mens en het museale binnenklimaat*, Erfgoedinspectie, March 2007
Martens, M.H.J., Schellen, H.L., Schijndel, A.W.M. van, Aarle, M.A.P. van, 2007, *Project Klimaatonderzoek Rijksmusea*, Technische Universiteit Eindhoven, February 2007
[together in one publication].

Baan, A., Duijnhoven, T.F.G. van, 2005, 'Analyse van het binnenklimaat in museum Het Mauritshuis te Den Haag', *Bouwfysica*, vol. 18, no 3/4, pp. 47-53.

- Gerrit Dou
Struick van der Loeff, L. and Groen, K., 1993, 'The Restoration and Technical Examination of Gerard Dou's *The Young Mother* in the Mauritshuis, *ICOM Committee for Conservation, 10th Triennial Meeting, Washington, 22-27 August 1993: Preprints*, ed. J. Bridgeland, London: James & James, Vol I, 98-103.

Boersma, A., 2000, 'Dou's Painting Technique: An Examination of Two Paintings', in R. Baer, *Gerrit Dou 1613-1675*, National Gallery of Art Washington [Exh. Cat.], pp. 54-63.

Languri, G., 2004, *Molecular Studies of Asphalt, Mummy and Kassel earth pigments*, PhD dissertation, University of Amsterdam, Molart Series (9), AMOLF, Amsterdam.

- Transferred/ghost/mirror images
Padfield, T., Erhardt, D., 1987, 'The spontaneous transfer of glass of an image of Joan of Arc', in: *ICOM Committee for Conservation, 8th Triennial Meeting, Sydney, 6-11 September 1987: Preprints*, ed. K. Grimstad, Getty Conservation Institute, Vol III, pp. 909-914.

Williams, S.R., 1988, 'Blooms, blushes, transferred images and mouldy surfaces: what are these distracting accretions on art works', in: *Proceedings of the 14th Annual IIC Conference-*

Canadian Group, Toronto, 27-30 May 1988, ed. J.H. Wellheiser, pp. 65-84.

Schilling, M.R., Carson, D.M., Khanjian, H.P., 1999, 'Gas chromatographic determination of the fatty acid and glycerol content of lipids. IV. Evaporation of fatty acids and the formation of ghost images by framed oil paintings', in: *ICOM Committee for Conservation, 12th Triennial Meeting, Lyon, 29 August-3 September 1999: Preprints,* ed. J. Bridgeland, London: James & James, Vol I, pp. 242-247.

Skaliks, A., 1999, *Blooming, Auswandern von Bindemittelbestandteilen aus ölhaltigen Farbsystemen: Phänomene, mögliche Ursachen und Überlegungen zur Prävention und Restaurierung,* Diplomarbeit, Fachhochschule Köln, [unpublished Masters thesis] pp. 25, 46-48, 63, 67, 148-151, 165, 173-174, 190-191.

- Fatty acid surface deposits

Koller, J., Burmester, A., 1990, 'Blanching of unvarnished modern paintings: a case study on a painting by Serge Poliakoff', in: *Cleaning, retouching and coatings: technology and practice for easel paintings and polychrome sculpture, Preprints of the contributions to the Brussels Congress,* 3-7 September 1990, eds. JS. Mills, P. Smith, London: IIC, pp. 138-143.

Burnstock, A., Caldwell, M., Odlyha, M., 1993, 'A technical examination of surface deterioration of Stanley Spencer's paintings at Sandham Memorial Chapel', in: *ICOM Committee for Conservation, 10th Triennial Meeting, Washington DC,* 22-27 August 1993: *Preprints*, ed. J. Bridgland, pp. 231-238.

Cox, H., 1993, 'The deterioration and conservation of chocolate from museum collections', *Studies in Conservation* 38, pp. 217-223.

Singer, B. Devenport, J. Wise, D., 1995, 'Examination of a blooming problem in a collection of unvarnished oil paintings', The Conservator, no 19, pp. 3-9.

Ordonez, E., Twilley, J., 1997, 'Clarifying the Haze. Efflorescence on works of art', *Analytical Chemistry: news and features and AC research,* pp. 416A-422A.

Van den Berg, J.D.J., 2002, 'Studies on the composition and formation of bloom on primed canvas used by F.E. Church and on paint in works of art by F. Stella', in: *Analytical chemical studies on traditional linseed oil paints,* PhD dissertation University of Amsterdam, Molart Series (6), AMOLF, Amsterdam, pp. 195-233.

Keune, K., Kirsch, K., Boon, J.J., 2007, 'Lead soap efflorescence in a 19th C painting: appearance, nature and sources of materials', *AIC Paintings Specialty Group, Annual Meeting in Providence, Rhode Island,* June 16-19, 2006: *Postprints, poster submissions*, compiler Mar Parkin, H., Vol. 19, pp. 146-150.

Van Loon, A., 2008, 'White hazes and surface crusts on dark oil paints', in: *Color changes and chemical reactivity in seventeenth-century oil paintings*, PhD dissertation University of Amsterdam, Molart Series (14), AMOLF, Amsterdam, pp. 119-203.

- Drying and ageing of oil

Boon, J.J., Peulvé, S.L., van den Brink, O.F., Duursma, M.C., Rainford, D., 1997, 'Molecular aspects of mobile and stationary phases in ageing tempera and oil paint films*',* in: *Early*

Italian Paintings. Techniques and Analysis, Symposium Maastricht, Limburg Conservation Institute, 9-10 October 1996, pp. 35-56.

Van den Berg, J.D.J., 1999, 'Chemical changes in curing and ageing oil paints', in: *ICOM Committee for Conservation, 12th Triennial Meeting, Lyon,* 20 August-3 September *1999: Preprints,* ed. J. Bridgeland, London: James & James, pp. 248-253.

Van den Berg, J.D.J., 2002, 'Oil paint: development stages from an oil to hard dry film', in: *Analytical chemical studies on traditional linseed oil paints,* PhD dissertation University of Amsterdam, Molart Series (6), AMOLF, Amsterdam, pp. 9-52.

Boon, J.J., Hoogland, F., Keune, K., 2007, 'Chemical process in aged oil paints affecting metal soap migration and aggregation', *AIC Paintings Specialty Group, Annual Meeting in Providence, Rhode Island,* June 16-19, 2006*: Postprints,* compiler Mar Parkin, H., Vol. 19, pp. 18-25.

Keune, K., Hoogland, F., Boon, J., Peggie, D., Higgitt, C., 2008, 'Comparative study of the effect of traditional pigments on artificially aged oil paint systems using complementary analytical techniques', in: *ICOM Committee for Conservation, 15th Triennial Meeting, New Delhi,* 22-26 September 2008: Preprints, London: James and James, Vol. II, pp. 833-842.

Norwegian Institute for Air Research
P.O. Box 100, N-2027 Kjeller, Norway
Associated with CIENS and the
Environmental Research Alliance of Norway
ISO certified according to NS-EN ISO 9001

REPORT SERIES SCIENTIFIC REPORT	REPORT NO. OR 42/2010	ISBN: 978-82-425-2251-1 (print) 978-82-425-2252-8 (electronic) ISSN: 0807-7207	
DATE 27.09.2010	SIGN.	NO. OF PAGES 164	PRICE NOK 150.-

TITLE PROPAINT Publishable Final Activity Report	PROJECT LEADER Elin Dalin NILU PROJECT NO. U-107013
AUTHOR(S) Elin Dahlin, Terje Grøntoft, Susana López-Aparicio, Marianne Odlyha, Mikkel Scharff, Tanja Larsen, Guillermo Andrade, Ana Tabuenca García, Antonio Ortega, Peter Mottner, Michal Obarzanowski, Janusz Czop, Roman Kozłowski, Maria Perla Colombini, Ilaria Bonaduce, David Thickett, Stephen Hackney, Jørgen Wadum, Anne Haack Christensen, Morten Ryhl-Svendsen, Sławomir Jakieła	CLASSIFICATION * A CONTRACT REF. SSPI- 044254

REPORT PREPARED FOR
European Commission

NILU

ABSTRACT
This report describes the work performed and the results achieved in the EU PROPAINT project (SSPI – 044254) (2007 - 2010). PROPAINT investigated the protection against gaseous air pollutants offered by microclimate frames (mc-frames) for paintings and the degradation of varnishes due to air pollutants. The results from PROPAINT were used to optimise design for microclimate control in mc-frames.

NORWEGIAN TITLE

PROPAINT. Publiserbar sluttrapport.

KEYWORDS		
PROPAINT	MC-frames, paintings	Effects

ABSTRACT (in Norwegian)
Denne rapporten beskriver arbeidet som ble utført og resultatene som ble oppnådd i EU prosjektet PROPAINT (SSPI - 044 254) (2007 - 2010). PROPAINT undersøkte mikroklima rammers (mc-rammer) beskyttelse av malerier mot forurensende gasser, og nedbrytning av fernisser på grunn av luftforurensning. Resultatene fra PROPAINT ble brukt til å optimalisere design for mikroklima kontroll og utforming av mc-rammer.

** Classification*
A Unclassified (can be ordered from NILU)
B Restricted distribution
C Classified (not to be distributed)

REFERENCE: U-107013
DATE: SEPTEMBER 2010
ISBN: 978-82-425-2251-1 (print)
978-82-425-2252-8 (electronic)

NILU is an independent, nonprofit institution established in 1969. Through its research NILU increases the understanding of climate change, of the composition of the atmosphere, of air quality and of hazardous substances. Based on its research, NILU markets integrated services and products within analyzing, monitoring and consulting. NILU is concerned with increasing public awareness about climate change and environmental pollution.

NILU
Norsk institutt for luftforskning
Norwegian Institute for Air Research

REFERENCE: U-107013
DATE: SEPTEMBER 2010
ISBN: 978-82-425-2251-1 (print)
978-82-425-2252-8 (electronic)

NILU is an independent, nonprofit institution established in 1969. Through its research NILU increases the understanding of climate change, of the composition of the atmosphere, of air quality and of hazardous substances. Based on its research, NILU markets integrated services and products within analyzing, monitoring and consulting. NILU is concerned with increasing public awareness about climate change and environmental pollution.

NILU
Norsk institutt for luftforskning
Norwegian Institute for Air Research