Molecular changes in egg tempera paint dosimeters as tools to monitor the museum environment
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Citation for published version (APA):
van den Brink, O. F. (2001). Molecular changes in egg tempera paint dosimeters as tools to monitor the museum environment
1. Introduction

This thesis reports research on the principle of paint-based dosimetry of museum conditions performed in the course of the EU supported ERA project (Environmental research for Art Conservation). The idea was tested to use the physico-chemical response of egg tempera paint to its environment as an indicator of the environmental stress. The first part of this chapter describes the rationale and approach of the research project. A variety of paint systems with different composition was prepared, cured and exposed under museum and laboratory conditions. These exposed paint systems play a central role in this thesis. A description of the preparation of the paints and their exposure conditions is therefore given in this chapter.

1.1 Rationale of the project

Painted works of art stored or displayed in museums and galleries are constantly subject to decay. The environment in the interior of a museum or historic building and the microclimate surrounding the object constitute a complex set of factors, which determines the nature and rate of decay. Such detrimental changes encompass not only discoloration of the varnish, but also discoloration of pigments and degradation of the binding medium. For example, Bacci et al. have observed a noticeable colour change in the "Predella della Trinità" by Luca Signorelli (1445-1523) on display in the Uffizi Gallery after a period of 66 months of regular exhibition to the public in the environmentally controlled Leonardo room [1]. Colour changes have also been observed in experimental paintings exposed in the National Gallery (London, UK) [2]. Important environmental factors are temperature, relative humidity, concentration of air pollutants, and light intensity and wavelength-distribution [3, 4]. Additional, less abundant but often much more harmful factors include vibration, insects and moulds, people and acts of God [4]. If the risk of damage on paintings were to be minimised, displaying them would be impossible and museums would lose part of their function. Cameron [4] describes this part of the museum's dilemma as follows: "People comfort is hazardous to works of art; one or the other must suffer." Hence, trade-offs have to be made. Depending on the materials present and provided the environment is understood, skilled and informed conservators
can to some extent retard the rate of deterioration of works of art. This can be achieved in a number of ways, for instance, by controlling physical environmental factors such as the temperature and relative humidity of the air. At great expense major museums direct much effort towards the standardisation of environmental conditions that surround works of art. In some cases new galleries or wings are thoroughly tested before use [5]. Maintaining a stable microclimate around a work of art, for instance, is probably the most effective method of protection, but widespread adoption of such methods will not occur until confidence is fully established and that will depend on a detailed understanding of the mechanisms of degradation due to environmental factors.

On the other hand not all art is well protected. Works of art are often stored in rooms with no climate control. Art on display in public buildings, historic buildings, palaces, churches and chapels is exposed to much larger environmental fluctuations. In particular where paintings are hung directly on external walls, large temperature and humidity fluctuations give rise to gradients, which affect the mechanical and chemical stability of the paint films. This may even lead to migration of organic constituents and cause blanching phenomena (for example in paintings by Stanley Spencer in the Sandham Chapel [6]). Such conditions require repeated interventions by trained conservators, which does not improve the condition and the overall stability of the works of art.

### 1.1.1 Model studies

In conservation science considerable attention is given to model studies on the effects of selected environmental factors on artists' materials. Hedley [7] has studied the effect of relative humidity on stress/strain response of genuine canvas samples of old paintings. Erhardt et al. [8] have investigated the effect of relative humidity changes on wooden panels and attempted to establish allowable relative humidity fluctuations. They have also determined expansion coefficients for typical layers of panel paintings, such as lead white oil paint, gesso and hide glue. This work has catalysed the development of thoughts on the issue of modelling painting behaviour and the establishment of new guidelines for museum conditions.

Due to the great interest of the paint industry, the colourfastness of dyes and pigments has been studied extensively. During the last decades, special devices have been used to expose paint systems to (very) high light intensities and/or specific weather conditions. Results obtained with such cabinets have contributed to the understanding of (some of) the variables which play a role in the fading of paintings [9]. More recently, devices were designed and constructed specifically to perform realistic light exposure model studies of materials used in...
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Saunders and Kirby have investigated light-induced damage to a variety of pigments [11]. In their study some pigments followed the reciprocity principle for light exposure, i.e. the degree of deterioration was determined by the product of exposure time and light intensity. In some cases however, the principle was not applicable. It must be noted that effects such as autocatalysis or the presence of an induction time may cause deviations from simple first order behaviour [12]. It was stated by Feller [12] that it is important that the degradation profile (kinetics of degradation) be understood when retarding of the degradation is an aim. To our knowledge apart from the efforts in the SCICULT project (partly published in [13]), no molecular model studies of light-induced deterioration of natural binding media have been carried out. Measurement of the light intensity can be relatively simple for artificially lit display areas. For side-lit interiors this is much more difficult. The intensity and wavelength distribution of the natural light is quite variable and depends on latitude, season, weather conditions and time of the day. Furthermore texture and reflectivity of the interior are important factors. As a result great variations in light intensity can occur within one room. Given this variation it is a very difficult task to predict the daylight dosages of objects in side-lit galleries [14], let alone to estimate the damage on those objects. However, given the fact that very high dosages (5% of annual recommendation) were measured after a single day of exposure in a side-lit gallery under sunny conditions [14], it is not surprising that great efforts are made to control the light intensity in galleries and in particular in historic buildings.

1.1.2 The chemical atmosphere

As early as 1850 the famous chemist and physicist Michael Faraday rang the alarm bell for the effects of sulphur dioxide on works of art, and suggested measures for the protection of paintings. In the 1960s attention was given again to the effects of air pollution on works of art. Holbrow [15] reviewed methods for the measurement of a variety of air pollutants and even reported results of exposure of fresh paint films to selected air pollutants at elevated levels. For example, sulphur dioxide was found to interfere with the drying process and lengthen the drying time of oil paint films, in extreme cases until ‘infinity’. Unfortunately, very little attention was paid to the effects on mature paint films. In 1965 Thomson reviewed possible effects of a variety of air pollutants on antiquities [16]. He suggested that scientific conservation research be carried out to determine the relative importance of the reduction of concentrations of dirt and pollutants for various classes of objects. More recently Baer and Banks [17], and Brimblecombe [18] have drawn the attention of conservation science and
atmospheric scientists to the effects of air pollutants on museum objects. Not only did these authors discuss the potential effects of pollutants, such as nitrogen oxides and sulphur oxides, that are imported into the museum from outside, they also mention pollutants of typical indoor origin, such as formaldehyde from wood and wood composites, and other building materials. In showcases pollutants that originate from the cases or their exhibits are a major concern. Comparison by Baer [17] shows that many standards for levels of pollutants can be applied, but these are rather arbitrarily determined. The effects of air pollutants such as nitrogen oxides ($\text{NO}_x$ and atmospheric nitric acid) [19, 20], sulphur oxides [21], peroxycetyl nitrate [22] and ozone [23-26] on organic dyes have been studied extensively by Grosjean and Cass and co-workers and molecular changes have been identified mainly by mass spectrometric studies [27].

1.1.3 Monitoring of the environment

Monitoring of pollutants in the museum environment has received more and more attention since the 1980s. The internal environment of the Tate Gallery, for instance, has been studied extensively, and concentrations of nitrogen oxides and sulphur oxides in this museum have been determined using various methods [28]. Similar investigations have been carried out at the Victoria and Albert museum (London, UK) [29]. Hisham and Grosjean [30] have studied the indoor and outdoor levels of nitrogen dioxide, nitric acid, and peroxycetyl nitrate in nine museums in Southern California. These studies clearly point to diurnal and seasonal variations in the levels of pollution. Variations in the values of relative humidity and temperature were investigated in a study of a museum microclimate in Padua by Camuffo [31]. The values were found to fluctuate considerably with season and the time of the day. Within the framework of the Uffizi Project [32] a comparative study of the air quality in two rooms of the Uffizi Gallery (Florence, Italy) has been carried out by Bernardi and Camuffo [33]. In their survey the temperature and relative humidity distributions were studied in detail and attention was given to particulate air pollution. Also within the Uffizi Project, De Santis et al. [34] have carried out monitoring of gaseous air pollutants, sulphur dioxide, nitric acid, nitrous acid and ozone. In this study, indoor and outdoor values were compared. At another site, this group investigated the relationship between indoor and outdoor levels of pollution [35] showing that the indoor levels of air pollution were greatly influenced by the magnitude of automotive traffic and by the weather conditions. Attention has also been paid to air pollution from indoor sources. At the V&A for instance, total volatile organic compound (TVOC) and formaldehyde concentrations were monitored in addition
The effectiveness of sealants to reduce VOC (formaldehyde, formic acid and acetic acid) emission from medium density fibreboard has been studied by Eremin and Wilthew [36]. A recent book by Camuffo [37] discusses in detail many physical factors that play a role in the micro-environments that surround objects of cultural heritage. It also deals with methods for monitoring of the microclimate.

The problem of dirt deposition on artefacts has been recognised since antiquity [38]. Dirt may originate from a variety of sources, and includes biological material from indoor or outdoor plants, soot from combustion, and fibres from visitor's clothes or cleaning activity. The visual quality of paintings can be affected by dirt deposition, or soiling. For instance, dark portions appear lighter due to surface scattering, and lighter portions can appear darker through absorption of light by the dust particles [39]. Recently Bellan et al. [40] determined the percentage surface coverage at which museum visitors can detect carbon black soiling of paintings. This percentage appeared to be higher than was previously thought. Apart from these visual effects, soiling may cause chemical effects, depending on the composition of the particles. It was determined that high acidity (or alkalinity) and in specific cases the iron content can have detrimental effects [38]. Scanning electron microscopy studies of paintings by Phenix and Burnstock [41] revealed that dirt may not only be present on the surface, but it may also be partially embedded in or even fully mixed with the surface coating of a painting. The mechanisms through which dirt deposition takes place are determined by factors such as size and texture of the particles. Camuffo [42] has discussed the particle deposition mechanisms that play a role in the soiling of murals, with a special focus on the temperature of the walls and the air. Murals differ from paintings in a few aspects. First of all, they are hung on a wall rather than part of it, so that they are more readily in the preferred state of thermal equilibrium with the ambient air. Secondly, they often have a different surface roughness. Nonetheless, the mechanisms that play an important role in the soiling of murals also apply to paintings, so that particle size, temperature gradients (in space) and density of the air must be considered important factors in the soiling of paintings too. Also the difference in polarity between surface and particle, and the relative humidity, which can increase the adhesion of the dirt particle by capillary condensation are important. The latter factor plays an important role at a relative humidity higher than 65% [41]. Hence it is not surprising that efforts are being made to keep dust away from paintings. These vary from the development of special framing methods to the placement of particle filters in the museum climate control installations. A very early example of efficient protection of paintings is an airtight frame designed by Simpson in 1892 [43]. As a matter of test one painting by Turner ("Venice") was placed in
the display case in the end of the last 19th century. Another painting by Turner (the seascape “Line Fishing off Hastings”), which was produced in the same period and had the same history as the first one was not placed in such a display case but exposed to the environment at the Victoria and Albert museum close to the one in the display case. In 1962 Bromelle [44] reported that “the picture (in the display case) appears to be in excellent condition without any of the yellowing or darkening which can often be seen in Turners of that period (c.1840).” At present a significant difference in the state of both paintings can be observed, which clearly indicates that the display case was very efficient in the protection of the painting [45].

1.1.4 Why paint-based dosimetry?

The internal environment of a building is subject to fluctuations. Hence, monitoring the quality of the museum environment by separate measurement of the individual factors that determine the museum environment at a particular point in time, however valuable, does not always yield a representative indication of the quality of the museum environment. Concentrations of indoor pollutants are often diluted with “fresh” air from outside the museum, which may cause them to drop below detectable (or alarming) levels, but does not take them away completely. Depending on their nature, such pollutants can still be detrimental due to cumulative effects.

Using dosimetry, factors that are not constant can be integrated over a longer period in time. Several dosimeters have been developed for specific purposes. Tennent and co-workers [46] developed an integrating dosimeter for ultraviolet light using the absorbance of a phenothiazine doped PVC-films, which increases proportionally with the dose of UV-light received by the foil due to transformation of the UV-sensitive phenothiazine. More recently, Leissner et al. [47-49] developed a dosimetric glass sensor that degrades as a function of the total experienced acidity during its exposure. Johansson et al. [50] developed a dosimetric system using metal strips to measure corrosivity in indoor environments.

Studies of the local museum environment mostly focus on a number of preselected factors, such as RH, temperature, light intensity and wavelength-distribution, or the monitoring of specific air pollutants, such as sulphur dioxide, nitrogen oxides and peroxyacetyl nitrate. A major disadvantage of separate measurements of environmental variables is that unexpected or exceptional factors can easily be overlooked. For example, during a routine conservation survey of the collection of the Herbert F. Johnson museum of Cornell University
an oily layer was discovered on many objects and display cases [51]. Mass spectrometric analysis of the material revealed that diethylaminoethanol (DEAE) had formed the oily layer. The volatile DEAE had been introduced into the museum environment by an open steam humidification system in which it was used as a corrosion inhibitor. Environmental monitoring by measurement of the concentrations of air pollutants can be compromised because some sources introduce a great variety of pollutants into the museum environment. Visitors, for instance, do not only change the relative humidity of the museum environment, they also change the chemical composition of the museum air as they release a wide range of organic compounds and inorganic gases [52].

A phenomenon that is often ignored in conservation science is that the effect of one factor may be greatly influenced by another. Some processes are inhibited by certain conditions, others are enhanced. There are factors which interact directly with each other to change the nature or reactivity of the museum environment and there are factors which are particularly harmful after some initial damage by another environmental factor has occurred on a painting. An example of the former is the effect of a combination of high relative humidity and NOx or SO2, which increases the acidity of the environment. As another example of interference of environmental factors, De Santis and Allegrini observed enhanced formation of sulphate (SO4^{2-}) from sulphur dioxide (SO2) by soot particles. This reaction strongly depends on the nature or the surface of the soot particles and is catalysed by the presence of nitrogen oxide (NO2) and elevated relative humidity [53]. Under these latter conditions the potentially harmful nitrous acid (HONO), which forms very reactive hydroxyl radicals (OH) upon photolysis by sunlight [54, 55] is also formed [53]. Carter et al. [56] found that the formation of hydroxyl radicals shows a linear dependence on light intensity and that it is further accelerated by increases in temperature and relative humidity. Clearly this latter example illustrates that the impact (reactivity) of the museum environment on works of art is made up of a complex combinations of the individual factors. Other examples include increased dirt adherence to paintings at elevated relative humidity [41], and enhanced photo-degradation at elevated relative humidity [57].

Fluctuations of temperature and relative humidity can play a role in two-step synergistic environmentally induced degradation processes, because they cause repeated shrinkage and expansion which ultimately leads to the formation of cracks. The material on the edges of the newly formed cracks is then exposed to the environment and can interact with light or air pollutants or can accumulate dust. If the cracks go deep into the painting they may expose underlying layers such as ground and preparatory layers. Such layers can be more sensitive to the micro-environment than the top layer(s). A calcium carbonate (CaCO3) ground for instance can react to the more voluminous and moisture sensitive calcium
sulphate (CaSO₄) upon exposure to humidity and sulphur oxides resulting in a new source of stress from within the painting. The formation of calcium sulphate (gypsum) from calcium carbonate (chalk), often referred to as fresco cancer has been observed in frescoes and is caused by SOₓ exposure [58]. Another possible example is the occurrence of blooming [6] (enforced by factors that accelerate hydrolytic processes), which changes the surface of a painting and makes it stickier and more sensitive to particle deposition.

These examples show that the effect of the environment on a work of art can not be considered simply as the integration of the effects of all the factors involved, but must be regarded as a complex more convoluted effect of various interacting factors. Therefore, monitoring the quality of the museum environment by separate measurement of the individual factors that constitute the museum environment, does not necessarily yield an accurate assessment of the damage done to the works of art on display. Moreover, most curators are less interested in the exact characterisation of the museum environment in terms of concentration of air pollutants, lighting conditions et cetera but rather in the question whether the museum environment implies potential danger for the museum collection, i.e. "Are the works of art really safe?"

1.2 Short description of the ERA project

Although the paintings themselves can be considered as dosimeters integrating all the effects of the environment, the deterioration of the physical and chemical condition of paintings can not be quantified easily. In the ERA project (project number EV5VCT94 0548 in the European Commission Environment Programme for the Conservation of Cultural Heritage) [59, 60], mock paintings take over this role and serve as dosimeters in which the compositional changes are related to environmental quality. Model paint systems have been prepared and exposed to extreme but controlled and well-defined environmental conditions in the laboratory. Mock paintings prepared with the same paint systems were also exposed to museum environments at selected field sites. Changes of the paints used in the mock paintings have been studied on the macroscopic, mesoscopic and molecular level by thermal and dynamic mechanical techniques (TGA, DMTA and DSC) [61-63], spectroscopic techniques (VIS and NIR) [64, 65] and mass spectrometric techniques [66-68]. The following subsections give details on the choice and preparation of the paint systems and their laboratory exposure. The field sites are described in a separate section. The section at the end of this
Chapter gives further information on the organisation of the ERA-project and places this thesis in the framework of the project.

1.3 Composition of the test systems based on egg tempera paint

1.3.1 The binding medium

Traditionally, paintings have been made with natural products, such drying oils, eggs, terpenoid resins, and natural glues. In the first stage of the development of a paint based dosimeter for museum conditions egg was selected as the binding medium, because it is the richest binding medium with respect to the variety of compounds and compound classes. The chemical composition of an average chicken egg as relevant to tempera painting is discussed in detail elsewhere [13, 69]. Eggs contain a large fraction of proteinaceous material. Proteins can undergo many alteration reactions, such as oxidation, $\beta$-elimination, alkylation and deamidation taking place on the amino acid residues, and cleavage of the peptide bonds. An overview of possible alteration reactions that proteinaceous materials can undergo is given by Boon et al. [13]. The second most abundant class is lipids, comprising cholesterol and glycerolipids, triglycerides and glycerophospholipids. These compounds can undergo oxidative reactions leading to a great variety of oxidation products depending on the degree of oxidative stress. Cholesterol for instance has many reactive sites, and many cholesterol alteration products are known in the literature [70-74]. Egg glycerolipids contain singly and multiply unsaturated fatty acid residues that all have their own reactivity towards oxidative stress. Depending on their degree of unsaturation, multiple oxygenation can occur, eventually leading to chain shortening [75]. Furthermore, triglycerides are sensitive to hydrolysis, ultimately leading to the formation of free fatty acids and glycerol.

Resin mastic was added to the egg binding medium for two reasons. First, it enhances the adhesive properties of the binding medium so that the paint adheres well to the relatively smooth surface of the inert Melinex® support. Secondly, it provides for another compound class that is not present in egg and it may provide potential marker molecules for processes that occur in terpenoid resins. Many components of mastic are known [76] and the ageing of triterpenoids has been studied at the FOM-institute in the framework of
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MOLART, a multidisciplinary project on Molecular Aspects of Ageing in painted Art [77, 78]. A mixture of egg and resin has been used in Italian painting practice [79].

1.3.2 The pigments

Added to the binding medium were inorganic pigments containing a variety of metal ions, such as lead white (basic lead carbonate), azurite (basic copper carbonate), smalt (glass sintered with cobalt), lead chromate, sienna (a mixture of \( \alpha \)-goethite, FeOOH, and \( \alpha \)-haematite, Fe\(_2\)O\(_3\)), Naples yellow (lead antimonate), and vermilion (mercuric sulphide, from Kremer). Paint systems were also prepared that contained organic pigments that are known to be sensitive to photodegradation and oxidation by air pollutants [21, 26]. These systems include indigo, curcumin and alizarin tempera. Azurite, smalt and vermilion were obtained from Kremer (Aichstetten, Germany), sienna and Naples yellow from Zecchi (Florence, Italy), and lead white and lead chromate from Aldrich (Steinheim, Germany). Alizarin and curcumin were from Acros (Geel, Belgium) and indigo was from Janssen (Geel Belgium).

1.3.3 Paint formulation and preparation of the test systems

The tempera binding medium was prepared by Roberto Belucci (restorer at the Opificio delle Pietre Dure, Florence, IT) following mostly the recipe reported in *Il libro dell’arte* by Cennino Cennini [80]. The yolk was separated from the white of an egg. The egg white was beaten so that a layer of foam formed on the liquid. After the egg white was left to stand overnight, the foam was separated from the liquid part of the egg white and discarded. The yolk was mixed with the remaining part of the egg white. To the egg were added three drops of apple cider vinegar and a solution of mastic in white spirit (Zecchi, Florence, IT), half the volume of the mixed egg. When pigmented tempera was prepared, the pigment was first ground with a few drops of water. Then the tempera binding medium was added, in some cases under addition of a few more drops of water to keep the paint easy to spread. The paint system was deposited on a sheet of Melinex\textsuperscript{®} using a using a Byk Gardner (Geretsried, Germany) film applicator at 200 \( \mu \)m wet layer thickness. The paint was allowed to cure for a period of three months in the dark before it was subjected to artificial ageing.
1.3.4 Artificial light ageing of the test systems

Light ageing was performed in an ageing facility at the Tate Gallery (London). Samples were exposed in the light-box for 4, 8, 16, 32 and 64 days. The ageing facility used 6 Philips TLD94 58 Watt daylight rendering fluorescent tubes that were filtered with a Perspex VE ultraviolet filter which has a cut-on wavelength at about 400 nm. Tubes were changed regularly to maintain a constant sample illuminance of about 20 klx. Cooling fans maintained the temperature at 4-5°C above ambient, and 5-10% below ambient relative humidity. Effectively, this yielded average values of 28-29°C and 27-28% relative humidity when the ageing was carried out. Light intensity during the exposure of the tempera test systems (May–June 1996) was 18,000 lx. Potential interference of pollutants in these experiments cannot be excluded, although in retrospect the Tate Gallery has the best air quality.

1.3.5 Thermal ageing

Thermal ageing was also carried out at the Tate Gallery. The samples were placed in an oven that maintained the temperature at 60°C and relative humidity at 55%. No light was admitted into the oven. The samples were exposed for 7, 14 and 21 days.

1.3.6 Exposure to SO₂ and NOₓ

Exposure to air pollutants was carried out at TNO (Delft, The Netherlands). The experimental set-up was used previously for the exposure of paper to air pollutants, and a detailed description is given by Havermans [81]. Samples mounted on A-4 size PMMA plates were placed in a gas chamber situated inside a climate chamber. During exposure the climate chamber was maintained the temperature at 23°C and relative humidity at 55%. Flows of SO₂, NOₓ, and air were tuned continuously so that the overall concentrations of SO₂ and NOₓ in the gas chamber were approximately 10 ppm and 20 ppm, respectively. Unlike light and thermal ageing, where samples were exposed for a range of times, the samples were exposed to NOₓ/SO₂ for a single fixed period of 4 days. Effectively, the average concentrations of SO₂ and NOₓ were 10.2 ppm and 16.7 ppm respectively during exposure.
1.4 Description of the field sites

Mock paintings were prepared that consisted of unexposed strips of the aforementioned formulations, mounted on a black background. **Figure 1** shows the design of these mock paintings. Identical dosimetric test systems, made according to this design, were simultaneously exposed at six selected sites for a period nine months, from mid December 1996 till the end of September 1997.

![Design of the mock painting with dosimetric test strips.](image)

**Figure 1.** Design of the mock painting with dosimetric test strips. The following paint systems were used: 1 unpigmented egg; 2 unpigmented egg + mastic; 3 lead white; 4 lead chromate; 5 curcumin; 6 sienna; 7 vermilion; 8 alizarin; 9 azurite; 10 smalt (Cobalt glass); 11 mastic resin and 12 Naples yellow (lead antimonate). Strips (65 x 9 mm) of the tempera paints on Melinex were mounted on a black support and framed.

These included major art galleries where the indoor environment was controlled, such as the Nightwatch room of the Rijksmuseum in Amsterdam, the Clore Gallery (Tate Gallery) in London, and the Uffizi Gallery in Florence, and two additional sites where the environment was not controlled, viz. Sandham Memorial Chapel at Burghclere (National Trust, England) and El Alcázar in Segovia (Spain). A dosimeter was also placed in the storage facility “Depot
Oost in the Rijksmuseum (Figure 2), where light levels are very low. An additional dosimeter served as a control and was stored at the FOM Institute for Atomic and Molecular Physics in an anti-corrosive bag (Preservation Equipment Ltd., Norfolk, UK) excluding oxygen and light.

The following subsections give a description of the field sites. For each of the field sites the exact location of the dosimeters in relation to the works of art on display is given, together with details of the light, temperature, RH, together with information on the environmental controls that are in place.

Figure 2 Photograph of a test painting (in circle) on a storage rack in the Rijksmuseum Depot “Oost”.

1.4.1 El Alcázar in Segovia (ALC)

El Alcázar in Segovia is Spain’s third most important monument and as such is a much visited site. The ERA dosimeter was exposed in the Cord Room. The dimensions of the room are 5.83m (h) x 10.60m (l) x 4.5m (w) and it has a stone floor and large windows.

During the exposure of the ERA dosimeters 417,461 people visited El Alcázar. There is no control or continuous monitoring of temperature and relative humidity in the Cord room. Data on the lighting, RH and temperature were obtained in the course of a number of visits during exposure of the ERA dosimeters. Some measurements were performed between 16th-23rd January 1997 and gave, in this unusually wet period, average values of 6.5°C and 84%.
Temperature and relative humidity values in spring were 17-23°C & 18-23% and in summer they were 24-28°C & 31-53%. Light levels were recorded each day during visits at about 1pm, with additional readings in the evenings before closing time. The lighting was unfiltered daylight and values at the site of the dosimeter varied from low levels of about 80 lx to close to 1000 lx. Blue wool standards indicated a total exposure of 450,000 lx h, which given the time of exposure, corresponds with 590 klx h/yr [82].

1.4.2 Rijksmuseum store room “Depot Oost” (RDO)

The depot “Oost” is located in the attic of the Rijksmuseum. Small glass windows in the long north wall of the room allow some daylight to enter. The room has concrete floors. The ERA dosimeter was placed in the middle of a rack for paintings, about 3m above the ground. There the dosimeter, like the paintings, can not be reached by direct sunlight, and light intensities are very low. Monitoring of UV and visible light intensity at the exact location of the dosimeter over a period of two days showed minimum and maximum light intensities of 2 and 12 lx at night and in the afternoon respectively, with UV light not being detected. The room is not connected to the central air-conditioning system, and RH is controlled by three “defensors” (mobile RH control units), although these devices are not always employed. Temperature is controlled by the central heating system. Relative humidity and temperature are monitored continuously (at 20 minute intervals). During the exposure of the ERA dosimeters, the average temperature was 22.7°C, with peaks of 29.2°C in August and 16.3°C on Christmas Day. Relative humidity varied between 28% at the end of December and 64% in mid May and the end of June 1997, with an average of 51.3%.

1.4.3 Rijksmuseum (RNW)

An ERA dosimeter was exposed in the Rijksmuseum, diagonally opposite the famous “Nightwatch” painting by Rembrandt, and in the upper left hand corner behind the painting “Corporaalschap van Kapitein Cornelis Bicker” by Joachim von Sandrart (1606-1688), Inv. no. 2117. During the nine months’ exposure of the ERA dosimeter, the Rijksmuseum had 848,791 visitors, the majority of whom would have entered this room. The room has wooden floors, partly covered with a cotton carpet (11 x 5 m, near the Nightwatch painting), and is partially illuminated by daylight entering through milk glass in the roof. The daylight is dimmed and directed by cloth in order to obtain a pleasing illumination of the works of art on display. Additional light comes from daylight rendering artificial light sources on the ceiling of the room. Illumination by these lamps (installed in
November 1996) is regulated (dynamic range 10-100%) by the output of sensors in the roof of the room, thus assisting the daylight illumination under cloudy or dark conditions. Light levels at the ERA dosimeter were less than 100 lx and no UV radiation was detected.

The room is air conditioned by means of a central dual duct VAV (variable air volume) system, that applies 70% air recirculation. The air inlet system uses EU-7 particle filters, but no chemical filtering is applied. Temperature and relative humidity are monitored at 8 minute intervals. The average temperature during the exposure was 20.5°C, with minimum and maximum values of 17.3°C, and 24.5°C, in March and August 1997, respectively. Average relative humidity was 53.4%. One relatively humid period was recorded (2 hours on 4th April 1997), when the RH was around 70%. The lowest RH (42%) was recorded on 23rd May 1997.

1.4.4 Sandham Memorial Chapel (SAC)

Sandham Memorial Chapel in Burghclere, Hampshire, contains a set of paintings by the British artist Stanley Spencer. During the period of exposure, about 8,200 people visited the chapel. The dosimeter was placed to the upper left of the painting “Sorting and Moving Kit-Bags” on the northeast facing wall. At this location the dosimeters, just like the painting, could be illuminated at a particular time of day by sunlight entering either one of the windows in the adjacent wall, provided that the Holland roller blinds were open, or through the main door, which opens directly to the external environment. Generally, the blinds are used to avoid high levels of illumination e.g. by direct sunlight. There is no total blackout when the Chapel is closed during the day, but also no electric light to supplement daylight on cloudy days. Under sunny conditions, this gave illumination levels of 33,000 lx. Cloudy weather with the blinds open yielded illumination levels of approx. 400 lx. Closing of the blinds under these conditions resulted in a significant reduction of the illuminance to values between 30 and 100 lx. Unfortunately, no data are available on the illuminance under sunny conditions with the blinds closed. Results on blue wool standards that were exposed in the Chapel alongside the tempera dosimeters indicate a total light exposure equivalent of 330 klx·h during the nine month exposure period [82]. Temperatures measured in the Chapel varied between 8.8°C in January and 21.1°C in July 1997. Values of relative humidity varied between 54% and 68%.
1.4.5 Tate Gallery (TAT)

The dosimeter at the Tate Gallery was exposed in the Clore Gallery (Room 103). This is a newly built extension, which was officially opened in 1987 and houses works of the 19th century British artist J. M. W. Turner. The number of visitors to the Clore Gallery during exposure of the dosimeter was estimated to be 190,000. Lighting is provided by a combination of low-UV fluorescent tubes and filtered daylight. During open hours the illumination is at a constant level of 200 lx. The lighting is switched off when the museum is closed. The Clore Gallery is also air-conditioned (dual duct VAV), with controlled relative humidity and temperature, and 85% air recirculation. Temperature variations were small, between 19-22°C and relative humidity averaged 50%. The air that is brought in by the air-conditioning system is filtered through particle filters (65% against BS test Dust No1.), and through activated carbon filters (TR 70).

1.4.6 Uffizi Gallery (UFF)

The ERA dosimeter was located in Leonardo’s room on a S-SW wall next to “The Baptism of Christ” (1472-1475, tempera on wood, Inv. 1890, No. 8358) by Andrea Verrocchio and Leonardo da Vinci and opposite the predella by Luca Signorelli on which colorimetric measurements have been performed [1]. More than one million people (1,044,350) visited the Uffizi during the nine months of exposure and it is likely that the majority of them visited the Leonardo’s Room. The floor of the room is brickwork treated to prevent the production of dust with wear, and vacuum cleaners are used regularly for cleaning. Light at the location of the dosimeter comes from both artificial sources and from a central skylight through milk glass (there are no windows in the room). Levels are nearly constant, with values of 120-150 lx in the visible region and 500-700 µW/m² in the UV-A region, which is below recommended limits [3]. The environment in the room is controlled by air-conditioning. The inlet is equipped with polyester particle filters and is mounted to the room ceiling. Air is collected at the bottom of the room, with 67% of the air being recirculated. Dehumidification occurs by means of the air conditioning cooling system, whilst humidification is achieved with an ultrasound humidifier equipped with an inverse osmosis demineralisation device. Temperature and relative humidity are monitored continuously. During the period of exposure of the ERA dosimeters, the temperature varied between 13-20°C in December 1996, and 22-30°C in August 1997, while the RH oscillated between 30% and 60%, in winter and spring, and between 40% and 64% in summer. The average temperature was 22°C, and the average value for relative humidity was 49%.
1.4.7 Summary of environmental conditions of the field sites

Table 1 summarises the indoor environmental conditions of the sites where the ERA dosimeters were exposed.

Table 1 Summary of the environmental data of the field sites.

<table>
<thead>
<tr>
<th>Site</th>
<th>RH (%)</th>
<th>T (°C)</th>
<th>Light intensity (lx)</th>
<th>UV intensity (μW/m²)</th>
<th>Number of visitors</th>
<th>Glass sensor AR [exp time]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALC</td>
<td>20-84</td>
<td>6.5-28</td>
<td>80-1000</td>
<td>7500 (UV-A)</td>
<td>417,461</td>
<td>0.036 [280 days]</td>
</tr>
<tr>
<td>RDO</td>
<td>28-64</td>
<td>16-29</td>
<td>2-12</td>
<td>0</td>
<td>Negligible</td>
<td>0.051 [189 days]</td>
</tr>
<tr>
<td>RNW</td>
<td>42-71</td>
<td>17-24.5</td>
<td>&lt;100</td>
<td>0</td>
<td>848,791</td>
<td>0.059 [189 days]</td>
</tr>
<tr>
<td>SAC</td>
<td>54-68</td>
<td>8.8-21</td>
<td>30-600&lt;sup&gt;(1)&lt;/sup&gt;</td>
<td>30 (UV)</td>
<td>8,200</td>
<td>0.034 [284 days]</td>
</tr>
<tr>
<td>TAT</td>
<td>40-60</td>
<td>19-22</td>
<td>&lt;200</td>
<td>0</td>
<td>190,000</td>
<td>0.0155 [168 days]</td>
</tr>
<tr>
<td>UFF</td>
<td>30-60</td>
<td>13-30</td>
<td>120-150</td>
<td>500-700 (UV-A)</td>
<td>1,044,350</td>
<td>0.04 [179 days]</td>
</tr>
</tbody>
</table>

For each site the relative humidity, temperature, intensity of visible light, intensity of UV radiation (when available), and the number of visitors during the nine month period of exposure are listed. The table also shows the average AR values determined for the glass sensors and their exposure time at the field sites. The AR value is a measure of the overall corrosivity of the environment. The principle of monitoring with glass sensors has been described by Leissner et al. [49]. Additional data on pollutant gases are given in Table 2. Specific information regarding the rooms where the dosimeters were exposed (such as type of air-conditioning and filtration) is summarised in Table 3.
### Table 2 Concentrations of pollutant gases (ppb) at the field sites.

<table>
<thead>
<tr>
<th>Site</th>
<th>NO₂</th>
<th>SO₂</th>
<th>HNO₃</th>
<th>O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALC</td>
<td>0-42 (O)</td>
<td>0</td>
<td>n.d.</td>
<td>0-33 (O)</td>
</tr>
<tr>
<td>RDO/RNW</td>
<td>35 (O)</td>
<td>2 (O)</td>
<td>n.d.</td>
<td>11 (O)</td>
</tr>
<tr>
<td>SAC</td>
<td>10-15 (O)</td>
<td>2-4 (O)</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>TAT</td>
<td>&lt; 2 (I)</td>
<td>&lt; 2 (I)</td>
<td>&lt; 2 (I)</td>
<td>&lt; 2 (I)</td>
</tr>
<tr>
<td>UFF</td>
<td>16-27 (I)</td>
<td>0.4-2.1 (I)</td>
<td>0.04-0.27 (I)</td>
<td>1-15 (I)</td>
</tr>
</tbody>
</table>

Conversion (1 ppb = )

<table>
<thead>
<tr>
<th>Site</th>
<th>NO₂</th>
<th>SO₂</th>
<th>HNO₃</th>
<th>O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALC</td>
<td>1.9 μg/m³</td>
<td>2.6 μg/m³</td>
<td>2.6 μg/m³</td>
<td>2.0 μg/m³</td>
</tr>
</tbody>
</table>

*NO₂ levels highest in winter, O₃ levels highest in summer (I) = indoor value, (O) = outdoor value, n.d. = not determined

### Table 3 Physical description of the field sites.

<table>
<thead>
<tr>
<th>Site</th>
<th>Climate control</th>
<th>Air filters</th>
<th>Room dimensions¹</th>
<th>Floor type</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALC</td>
<td>None</td>
<td>None</td>
<td>10.6 x 4.5 x 5.8 {277}</td>
<td>Stone</td>
</tr>
<tr>
<td>RDO</td>
<td>Central heating and mobile RH control units</td>
<td>None</td>
<td>{578}</td>
<td>Concrete</td>
</tr>
<tr>
<td>RNW</td>
<td>Air conditioning</td>
<td>Particle filters</td>
<td>14.5 x 20 x 8 {2320}</td>
<td>Wood, carpet</td>
</tr>
<tr>
<td>SAC</td>
<td>Heating by radiators</td>
<td>None</td>
<td>9.4 x 5.2 x 7.9 {386}</td>
<td>Stone</td>
</tr>
<tr>
<td>TAT</td>
<td>Air conditioning</td>
<td>Particle and carbon filters</td>
<td>10 x 6 x 5 {300}</td>
<td>Wood</td>
</tr>
<tr>
<td>UFF</td>
<td>Air conditioning</td>
<td>Particle filters</td>
<td>11.6 x 11.3 x 7 {917}</td>
<td>Brick</td>
</tr>
</tbody>
</table>

¹L x W x H (m) {volume (m³)}
1.5 The ERA-project and the scope of this thesis

As outlined in Figure 3, the development of a paint-based dosimeter for environmental conditions was pursued in two phases. Firstly, the concept was tested using artificial exposure, such as accelerated artificial light ageing, thermal ageing and exposure to high concentrations of air pollutants (NO\textsubscript{x} and SO\textsubscript{2}). The exposed test systems were analysed by the three partners in the project. In this stage analysis by ancillary techniques was also started. The results allowed identification of some of the ageing processes and facilitated interpretation of the data obtained from direct temperature-resolved mass spectrometry (DTMS). The results of the analysis of the laboratory exposed paint systems were used to decide on the duration of exposure at the field sites.

Figure 3 Organisation of the ERA-project. OPD, Opificio delle Pietre Dure, Florence; Tate, Tate Gallery, London; TNO, Nederlandse organisatie voor Toegepast Natuurwetenschappelijk Onderzoek, Delft; Bbk, Birkbeck College London University; AMOLF, FOM Institute for Atomic and Molecular Physics; IROE, CNR Istituto di Ricerca sulle Onde Elettromagnetiche; MS, mass spectrometry; TA, thermoanalysis; FTIR, Fourier transform infrared spectroscopy; VIS, visible light spectroscopy.
Chapter 1

The mock paintings made from the tempera test systems were exposed for a period of nine months. After exposure, the mock paintings were analysed by the three partners of the project using the same analytical techniques and the results obtained were compared with those from the laboratory-exposed dosimeters. In the case of DTMS analysis, for instance, the set of light-aged samples served as a calibration set. Eventually, all dosimetric data obtained by each of the techniques were compared to the conventional environmental data on the field sites.

This thesis focuses on the mass spectrometric work carried out on paint samples taken from the dosimeters. It reports the work carried out at the FOM Institute for Atomic and Molecular Physics in the framework of the project. Chapters 2 to 4 focus on paint-based dosimetry of the museum environment and the methodology applied to read out the dosimetric test systems. Chapters 5 to 7 describe the investigation of the chemical changes in the tests systems in molecular detail. The results obtained allowed the identification of some of the ageing processes of the egg binding medium and facilitated interpretation of the DTMS data.

Chapter 2 describes the methodology that was applied to determine the degree of chemical change in the test systems by DTMS and discriminant analysis (DA). Chemical changes were observed by DTMS analysis of the laboratory-exposed dosimeters that could be correlated with the light ageing time using DA. Chapter 2 also shows that the same methodology can be used to discriminate the various chemical processes in the paint-based dosimeters, such as those induced by light exposure and those induced by exposure to NO\textsubscript{x}/SO\textsubscript{2}.

The first part of Chapter 3 describes the results of a test procedure that was developed to determine the efficacy of each of the test systems. The second part describes the results obtained by DTMS and DA of the laboratory-exposed and field-exposed dosimeters per test system. It is demonstrated that the chemical composition of the binding medium of a tempera paint is determined by its pigments. It is also found that the different test systems respond differently to the same environmental conditions.

An overall interpretation of the dosimetric results obtained by DTMS and DA of the field-exposed test systems is given in Chapter 4. This chapter also includes a report of a paint-based dosimetry survey that was carried out at nine sites in the Rijksmuseum (Amsterdam, The Netherlands).

The most important organic chemical changes observed in the test systems by DTMS were further investigated using ancillary techniques such as DTMSMS, size exclusion chromatography (SEC), matrix-assisted laser desorption/ionisation Fourier transform ion cyclotron resonance mass spectrometry (MALDI-FTMS),
and electrospray ionisation (ESI-) FTMSMS (see also Figure 3). This research was mainly performed on samples of the egg-only test system.

The degradation of cholesterol was studied by DTMSMS. The results reported in Chapter 5 indicate that 7-ketocholesterol, 5,6-epoxycholestan-3-ol and cholestenediol are rapidly formed from cholesterol upon light ageing. The chances that cholesterol can be found intact in aged tempera paintings are minimal.

Chapter 6 reports the results obtained by MALDI-FTMS of solvent extracts of the laboratory-exposed egg-only test systems. Oxygenation and oxidative cleavage reactions of unsaturated fatty acid moieties were identified in the ageing of triacylglycerols and diacylphosphatidylcholines. SEC results also reported in this chapter show that cross-linking plays a role in the light ageing process.

ESI-FTMS(MS) was used to study the chemical changes in the glycerolipid fraction in more detail. It is demonstrated in Chapter 7 that this technique can be used to monitor the degree of hydrolysis of triacylglycerols. This chapter also shows that tandem mass spectrometry with high resolution in broadband mode can be used to determine the fatty acid speciation of natural and oxidised triacylglycerols.

Recommendations for further development of paint-based dosimetry for environmental monitoring of museums are presented in Chapter 8.

References


Chapter 1


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52 Wang, T. C., 'A study of bioeffluents in a college classroom', ASHREA Transactions 81 (1975) 32-44.


Chapter 1


Introduction


