Molecular changes in egg tempera paint dosimeters as tools to monitor the museum environment
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4. Dosimetry of the environment in various museums: Interpretation of the results of the field studies

In the previous chapter the results of paint-based dosimetry obtained on nine paint systems exposed at five different sites in Europe were presented. The results were shown as bar graphs and shortly discussed. This chapter presents the results in a different way, viz. as ranking of the sites. This allows comparison of the sites and the identification of test systems that show similarities in their response. In a survey performed at nine different sites in the Rijksmuseum (Amsterdam, NL), paint-based dosimeters were exposed for a shorter period than in the European survey. The results of the survey at the Rijksmuseum are reported in section 3 of this chapter. The conclusions of the two surveys are summarised in the fourth section of this chapter.

4.1 Introduction

4.1.1 The nature of the chemical changes observed in paint-based dosimeters

The lipid fraction of the egg tempera binding medium, that consist of egg triglycerides and cholesterol, and triterpenoids from mastic is detected with greatest sensitivity by DTMS. The proteinaceous fraction of the egg is observed as fragments that result from pyrolysis of the proteinaceous macromolecules. DTMS indicates that the inorganic pigments catalyse the oxidation of the lipid fraction as early as the curing stage. Oxidation products are not observed in the cured unpigmented and organic pigmented test systems. Upon light ageing chemical changes in the lipid fraction of the tempera binding medium are observed. An important process is the oxidation of (poly)unsaturated fatty acid residues in glycerolipids. Hydrolysis of the glycerolipids takes place upon light ageing of the unpigmented tempera. Chemically, enhancement of hydrolytic
processes can be related to a higher moisture content and/or higher temperatures. Test systems with inorganic pigments are more sensitive to the effect of relative humidity due to their ability to bind water by direct interaction with the pigment. A process generally observed upon ageing is the oxidation of cholesterol to 7-ketocholesterol, and oxo-cholesterol. The triterpenoids in the mastic fraction undergo specific side-chain oxidation processes upon light exposure.

Exposure to NO\textsubscript{x} and SO\textsubscript{2} in the dark for four days leads to similar alteration processes in the lipid fraction, although in some cases differences are observed. Hydrolytic processes, for instance, are more prominent under NO\textsubscript{x}/SO\textsubscript{2} conditions; cholesterol on the other hand is less severely oxidised. Furthermore, in some cases NO\textsubscript{x}/SO\textsubscript{2} exposure leads to the formation of sulphates or sulphonic acids. On the other hand, in most cases thermal ageing in the dark for up to 21 days does not result in significant changes of the mass spectra.

The degree of chemical change in the light-exposed tempera dosimetric test systems correlates well with the duration of light exposure. The results of field exposure show that the chemical composition of the paint is changed by exposure in museums: significant differences in chemical composition are observed among test systems exposed in different field sites.

The processes that are observed upon field exposure of the test systems are most similar to those occurring upon light ageing, and hence the light ageing sample series was used for calibration of the degree of chemical change. Only in the case of lead white tempera, discriminant analysis detects that the chemical changes occurring upon field exposure differ significantly from those observed upon light ageing. Although the difference is observed in the first discriminant function, this does not lead to a difference in the classification of the field sites. In some other inorganic pigmented test systems the field-exposed dosimeters are distinguished from the light ageing series by the less significant second discriminant function. Enhanced hydrolysis has been identified as one of the reasons that the field exposure processes differ from those occurring during light ageing.

4.1.2 Quantification of the chemical changes in the paint-based dosimeters

The tempera light ageing series were used successfully to calibrate the degree of chemical change in the field-exposed tempera dosimeters. As the light ageing set was used for calibration, the degree of chemical change in the thermally aged test systems and the NO\textsubscript{x}/SO\textsubscript{2} exposed test systems can also be expressed in terms of
light ageing equivalents (LAE). In general the thermally aged test systems show a negligible light ageing equivalent, except for the sienna tempera, which displays a low light ageing equivalent of less than 8 days. The test systems are more changed upon exposure to NO\textsubscript{x}/SO\textsubscript{2}, showing LAEs between a minimum of less than 8 days for lead white and much more than 64 days in the case of sienna. On the basis of the LAEs of the NO\textsubscript{x}/SO\textsubscript{2} exposed dosimeters the different test systems can be grouped as follows:

- low sensitivity to NO\textsubscript{x}/SO\textsubscript{2} (LAE < 16 days):
  - lead white, alizarin, and smalt
- medium sensitivity to NO\textsubscript{x}/SO\textsubscript{2} (16 < LAE < 32 days):
  - unpigmented, lead chromate, and egg only
- high sensitivity to NO\textsubscript{x}/SO\textsubscript{2} (LAE > 32 days):
  - curcumin, Naples yellow, and sienna (extremely)

4.2 Paint-based dosimetry at five European museums

4.2.1 Summary of the dosimetric results

In the previous chapter average (n=3) values of the degree of chemical change were presented, and the significance of differences in degree of chemical change was shortly discussed in terms of discriminatory power of the dosimetric results. As the nature of the chemical change in the test systems differs from test system to test system, direct comparison of the degree of chemical change (score on the first discriminant function) is not useful. Therefore, in this summary the ranking order of the exposure sites is given per test system. The presentation of the ranking order takes into account the significance of the difference in degree of chemical change. Sites are given the same rank when the ranges of scores of triplicate measurements partly overlap. Such overlap can be caused by either a low discriminatory power of the dosimeter or a high degree of similarity in chemical composition of the test system after exposure in the sites.

Table 1 summarises the ranking results that have been obtained with each of the field-exposed tempera dosimeters. The ranking position of a site is given as a number between one (least chemical change) and six (largest chemical change). In the case of overlap more than one rank number is given. For
comparison, the degree of chemical change of the 64-day light-aged sample is given in the second column of the table. In order to provide an indication of the sensitivity of a test system towards NO\textsubscript{x}/SO\textsubscript{2} exposure, the degree of chemical change in the dosimeter that was exposed to these gases is expressed as LAE and shown in the third column of the table. In some cases the degree of chemical change in a field-exposed dosimeter or in a NO\textsubscript{x}/SO\textsubscript{2} exposed dosimeter exceeded that of the 64-day light-aged dosimeter. These cases are highlighted as bold in Table 1.

Table 1  Ranking of the exposure sites based on the dosimetric results obtained by DTMS.

<table>
<thead>
<tr>
<th>Test system</th>
<th>64L</th>
<th>NOX</th>
<th>ALC</th>
<th>RDO</th>
<th>RNW</th>
<th>SAC</th>
<th>TAT</th>
<th>UFF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Egg-only</td>
<td>2.4</td>
<td>32</td>
<td>6</td>
<td>1</td>
<td>5</td>
<td>4</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Unpigmented</td>
<td>2.95</td>
<td>&gt;16</td>
<td>6</td>
<td>2</td>
<td>4</td>
<td>5</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Alizarin</td>
<td>2.8</td>
<td>&lt;16</td>
<td>3</td>
<td>1</td>
<td>4</td>
<td>6</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Curcumin</td>
<td>2.9</td>
<td>&lt;64</td>
<td>3</td>
<td>2</td>
<td>6</td>
<td>1</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Lead white</td>
<td>2.6</td>
<td>&gt;8</td>
<td>4</td>
<td>3</td>
<td>6</td>
<td>1</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Sienna</td>
<td>2.6</td>
<td>&gt;&gt;64</td>
<td>3</td>
<td>2</td>
<td>4</td>
<td>1</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Smalt</td>
<td>2.5</td>
<td>&lt;16</td>
<td>3</td>
<td>2</td>
<td>6</td>
<td>1</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td>2.6</td>
<td>&gt;16</td>
<td>2</td>
<td>4</td>
<td>4</td>
<td>1</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>chromate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naples yellow</td>
<td>2.8</td>
<td>&gt;64</td>
<td>2</td>
<td>4</td>
<td>4</td>
<td>1</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>

| dce = degree of chemical change (A.U.); LAE$^+$ = light ageing equivalent (days) |
| bold = value exceeds that of the 64-day light-aged dosimeter. |

4.2.2 Interpretation of the dosimetric ranking results

The dosimetric results obtained with the field-exposed dosimeters can be divided into two groups. The first group is those of the unpigmented and organic pigmented temperas, of which the field-exposed dosimeters all show degrees of chemical change that fall within the light ageing calibration set. The second
Dosimetry of the environment in various museums

group is that of the inorganic pigment temperas, where the dosimeters exposed at the “worst” sites show degrees of chemical change, which exceed the dynamic range of the light ageing calibration set (i.e. the degree of chemical change in the 64-day light-aged sample).

A few general observations can be made that apply to each of the exposed test systems. Firstly, the degree of chemical change observed in the dosimeters that were exposed at the Rijksmuseum Depot “Oost” strongly suggests that environmental factors other than light contribute to chemical changes in the dosimeters that were exposed at this site. The high ΔR value of the RDO exposed glass sensor, which measures the corrosion of glass (Chapter 1, Table 1), supports the hypothesis that the air quality induces the chemical change in the Depot “Oost” dosimeters. Further investigation is necessary to determine which factor at the Rijksmuseum leads to these severe changes in the chemical composition of the test systems. The RDO was also included as one of the sites in the 3-months survey at the Rijksmuseum (vide infra). Second, there is a general observation that the dosimeters exposed at the uncontrolled environments of the Alcázar and Sandham Chapel classify among those with the largest chemical change. Clearly, many factors are present in these uncontrolled environments that may lead to accelerated degradation. Firstly, the relative humidity and temperature fluctuate strongly. Then, the light intensity is not in agreement with museum standards and, possibly more importantly, the intensity of UV light may be considerably higher than in the controlled museum sites.

The dosimeters of the unpigmented and organic pigmented temperas that have been exposed in the Depot “Oost” of the Rijksmuseum all rank among those with the lowest degree of chemical change compared with the dosimeters of the same test systems that were exposed at the other field sites. This is probably due to the fact that the Depot is a dark site. Thus the results suggest that light intensity is an additional important factor in the deterioration of the unpigmented and organic pigmented test systems.

The observation on the inorganic pigmented temperas that the degree of chemical change in the dosimeters exposed at the “worst” sites exceed the light ageing calibration set immediately addresses the question of the validity of the reciprocity principle for light ageing. Often, in the inorganic pigmented systems, hydrolysis is identified as an important component of the light ageing process. In some of the test systems enhanced hydrolysis has been identified as one of the reasons that the field exposure processes differ from those occurring during light ageing. Chemically, enhancement of hydrolytic processes can be related to a higher moisture content and/or higher temperatures. Test systems with inorganic pigments are more sensitive to the effect of relative humidity due to their ability to bind water by direct interaction with the pigment.
Chapter 4

The consistent observation on the field-exposed inorganic pigment temperas that the Tate Gallery dosimeter classifies as the one with the smallest degree of chemical change confirms the above line of reasoning. As shown in Chapter 1, the Tate Gallery (Clore Gallery) is the best-controlled site regarding temperature and relative humidity. Not only the average humidity during exposure but also the fluctuations in relative humidity and temperature are thought by repeated expansion and shrinkage to influence the craquelure formation and hence accessibility of the paint for reactive species. SEM results [1] showed that crack formation plays a role in the tempera test systems. Light intensities in the Rijksmuseum Nightwatch room and the Uffizi Gallery are equal to or lower than those in the Tate Gallery. However, they have less well controlled relative humidity and temperature. This may explain the higher degree of chemical change in the RNW and UFF exposed dosimeters. Another cause of the difference observed may be that the Tate Gallery is the only site where the inlet air for the air conditioning system is filtered through carbon filters to remove air pollutants. Furthermore, the number of visitors in the Clore Gallery (Tate Gallery) is considerably lower than in the Uffizi Gallery and the Rijksmuseum Nightwatch room. Supporting evidence that the air quality plays an important role in the deterioration of the dosimeters comes from the comparison of the results obtained on the respective field-exposed inorganic dosimeters. The number of field-exposed dosimeters which score a light ageing equivalent of more than 64 days varies strongly among the inorganic pigmented test systems. In fact the number of sites that have an LAE higher than 64 days seems to correlate with the sensitivity of the test system towards NO$_x$/SO$_2$. In the case of the test systems which show a low sensitivity to NO$_x$/SO$_2$, viz. the lead white and smalt temperas, the number of field-exposed dosimeters that have an LAE of more than 64 days is small compared to the sensitive Naples yellow and sienna temperas. Clearly, further research and comparison of dosimetric results with conventional environmental data is necessary to resolve this question. The following section presents results of a survey at nine sites in the Rijksmuseum, which included an attempt to address the effect of the museum air quality on the dosimeters.
4.3 Paint-based dosimetry at nine sites in the Rijksmuseum

4.3.1 Introduction

The rationale behind a survey of nine different sites at the Rijksmuseum was twofold. First, as discussed above, the results of the field study at the five European sites indicated that the degree of chemical change in the dosimeters exposed in the Rijksmuseum was much higher than expected. The staff of the Rijksmuseum suggested as explanation that the climate in some rooms in the museum, viz. the older part of the building, could be of worse quality than the air in the newer part of the building. Hence, a new survey was planned at the request of Dr. A. Wallert and H. Kat of the Rijksmuseum Conservation Department. In this survey sensors were exposed in the older as well as in the newer part of the museum. Secondly, as the effects of nine months’ exposure were already severe, shorter exposure of the mock paintings was thought to be advantageous and could lead to enhancement of the differences in degree of chemical change among the sites. Therefore, the dosimetric mock paintings in the new survey were exposed for a period of 3 months (97 days).

4.3.2 Description of the exposure sites and monitor design

The nine exposure sites in the Rijksmuseum are described in Box 1. At two of the sites, i.e. the Library and the Nightwatch room, two mock paintings were exposed, one unshielded and one shielded from the light, in order to assess the effect of the air composition.

The exposed mock paintings consisted of 4 dosimetric test strips of egg tempera paint on Melinex, of which one was unpigmented, another one was pigmented with alizarin, and two were pigmented with the inorganic pigments azurite and lead chromate. The strips were cut from the same batch of tempera paint as the ones used for the first field study, and hence had identical composition. Their dimensions were 9 x 25 mm (azurite and unpigmented) and 9 x 35 mm (lead chromate and alizarin). They were attached to the same black polymer support material as used in the first set of test systems. Selection of the temperas was based on availability of spare material that was not consumed in laboratory testing and field exposure. Figure 1 shows one of the mock paintings exposed in the study collection of the Rijksmuseum.
Box 1  

Description of the nine exposure sites in the Rijksmuseum.

1. Office Dr. Arie Wallert in “Villa” (OVI), no air, dosimeter placed in window sill facing outside.
2. “Villadepot” (RDV), rack 315, independent air-conditioning, RH and T controlled, very low light intensity, (dark)
3. Depot “Oost” (RDO), in old building, rack 235, same site as in previous exposure, controlled by defensors light intensity very low (2-12 lux)
4. Depot “Zuid” (RDZ), in newer South wing, rack 515, independent air-conditioning RH & T control, very low light intensity (dark)
5. Study room (STU), old building, next to Tüchlein by Pordenone, central air-conditioning, big room, artificial light (UV filtered TLs).
6. Library (Lib), in old building, upper walkway. One dosimeter exposed to the light (Lib L) and one shielded from the light (Lib D). No air-conditioning, combined artificial and daylight.
8. Nightwatch room (NW), old building, behind painting by Sandrart, same site as in previous exposure. One dosimeter exposed to the light (NW L) and one shielded from the light (NW D). Central air-conditioning, controlled RH and T, normal museum lighting intensity.
9. Room 205, old building (205), horizontally placed above a painting by Van Heemskerk. The light intensity is higher than in the Nightwatch room.

4.3.3 Results

After exposure, the unpigmented tempera test strips were analysed according to the methodology described in Chapter 2. Figure 2 shows the results obtained for the unpigmented tempera dosimeters. The degree of chemical change in the 16-day light-aged unpigmented tempera sample is also shown in this figure for reference. The difference in degree of chemical change between the NW L and the RDO exposed dosimeter in this assay is larger than in the assay with 9 months’ exposure time. This supports the notion in Chapter 3 that a better discrimination can be obtained with the unpigmented tempera test system when shorter exposure times are used. The results clearly indicate that there is a large
difference in quality among the depots. Exposure in the Villa depot (RDV) leads to largest chemical change observed for the depots, and the Depot Zuid (RDZ) leads to the lowest degree of chemical change.

Differences between dosimeters that have been exposed in the exhibition rooms are less pronounced. The dosimeter exposed in the department Textilis (TEX), which is located in the newer South wing of the building shows the smallest degree of chemical change. Together with the result obtained on the RDZ dosimeter, this is interpreted as an indication that there is a difference in the quality of the museum conditions between the older part of the building and the South wing. The dosimeter exposed in room 205 shows the largest degree of chemical change of dosimeters exposed in exhibition rooms. This may be caused by the fact that the dosimeter was placed horizontally. Visual inspection of the dosimeter by microscopy revealed that it had collected dust on the surface. The dust may have acted as a catalyst of the deterioration processes and thus may have led to the high degree of chemical change.

The degree of chemical change observed in the dark exposed dosimeters from the Nightwatch room (NW L) and the Library (Lib L) is very small. This indicates that either the activation by light plays a decisive role in the ageing processes or that the design of the box for light shielding hampers the free flow of air and hence understates the influence of the air quality on the chemical composition of the test system. Additional experiments are required to resolve this matter.
Chapter 4

Unpigmented tempera

![Graph showing DF1 scores for unpigmented tempera dosimeters exposed in the field study at the Rijksmuseum.](image)

Figure 2  Scores on the first discriminant function for unpigmented tempera dosimeters exposed in the field study at the Rijksmuseum.

As expected the sensor exposed in the uncontrolled Villa office (OVI) shows the highest degree of chemical change. It plots higher than the 16-day light-aged unpigmented tempera. There are many factors that can explain this high score. First, the light intensity in the windowsill can be very high on sunny days and the sensor may even be exposed to direct sunlight through glass. Hence, the high UV intensity may also have lead to extreme ageing in this test system. In addition, the relative humidity and temperature in the room are not controlled.

4.4 Conclusions of the two dosimetric field studies

4.4.1 European survey

The controlled museum environments have less affected the chemical composition of lipid components of the egg tempera dosimetric test systems compared with the uncontrolled museum environments.

The Tate Gallery exposure site, which has the best-controlled relative humidity and temperature and uses carbon filters for the inlet of the air-
conditioning system, shows the smallest degree of chemical change in the inorganic pigmented temperas.

There are strong indications that the air quality plays an important role in the environmentally induced chemical change in the paint-based dosimeters.

The test systems that do not contain inorganic pigments, viz. alizarin, curcumin, unpigmented and egg-only tempera, display a higher relative sensitivity to light (dosage) than the inorganic-pigmented temperas.

4.4.2 Rijksmuseum survey

Exposure of unpigmented tempera paint-based dosimeters for a shorter period than in the first field study also results in a good differentiation among the exposure sites. Moreover, the difference between the two sites that were also included in the first field study were enhanced upon reduction of the exposure period. Given the high degree of chemical change in the inorganic pigmented dosimeters that were exposed for nine months in the first field study, it is expected that short-term exposure of these test systems will also give good results.

The results obtained in the survey confirm the notion of a difference in the quality of the museum environment between the older part of the Rijksmuseum and the newer South wing.

Reference
