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Dosimetry of paintings: determination of the degree of chemical change in museum exposed test paintings (lead white tempera) by thermal analysis and infrared spectroscopy

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Abstract

Thermoanalytical (DSC and TGA) data on the basic lead carbonate pigment alone have been previously published [J. Chem. Soc., Dalton Trans. (1996) 3639]. This paper draws attention to the modifying effect of basic lead carbonate on the thermal stability of the paint medium, and on the degradation of the paint medium under controlled light ageing conditions. The various light dosages received by the samples were found to produce differences in the shape of the leading edge of the DSC curves. Quantification of the data shows that there is a systematic trend, i.e. the difference in the leading edge of the DSC curve, with respect to the control sample, increases with the duration of light exposure of the samples. In the natural ageing of the samples exposed in various galleries for a period of 9 months, the dominant change is a shift in the overall peak. Changes in artificially and naturally aged samples were also identified by Fourier transform infrared spectroscopy. The broadening of the carbonyl peak due to the formation of lipid oxidation products could be quantified to determine the degree of chemical change. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: DSC; FTIR; Basic lead carbonate; Dosimetry; Artificial ageing; Natural ageing

1. Introduction

Painted works of art on display in museums are inevitably subject to changes with time. For example, in the work of the English artist, J.M.W. Turner, there are instances of ageing and darkening of the medium, and the formation of surface cracks which have caused changes in the appearance and tonality of the paintings [2]. The observed fading of colours has led to the development of colour measurement of paintings [3,4] and also research into the effect of light exposure [5,6] and relative humidity on pigment fading in prepared paint samples [7]. It appears that the chemical nature of the binding medium also influences the rate of fading [7].

DSC studies have been previously performed on a number of lead white tempera pigmented samples from paintings. The exothermic degradation curves of samples from 13th to 16th century Italian paintings (Fig. 1) were found to be of the following shape [8]. The main peak occurred at about 270°C and there was a smaller peak at higher temperatures. For the lead white tempera prepared in this project the shape of the DSC curve was distinctly different. From previous work on the lead white pigment itself [1] it was found that the prepared samples showed contributions from

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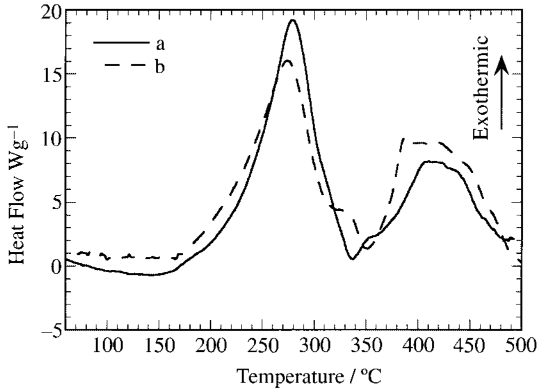

Fig. 1. DSC curves obtained from samples heated in O_2 at 40°C/min of (a) 16th century Italian painting by Francesco di Giorgio di Martini "Nativity of Christ" (ca. 1500), and (b) 13th century painting "Madonna del Popola" by Coppo di Marcovaldo in the Capella Brancacci, Chiesa S. Maria del Carmine, Florence, Italy).

the pigment. In this paper the shape of the curve will be discussed in relation to varying pigment content.

Lead white was selected as a pigment because of its widespread occurrence in old paintings, being one of the commonest white pigments before the introduction of titanium white in the 20th century. It is often found in combination with other colours, e.g. with red pigments in the tones of flesh, or with blue in the tints of skies [9]. Lead white was also chosen owing to its known catalytic effect in speeding up ageing processes, so that its presence could give useful information after artificial ageing. The lead white pigment is one of the oldest known synthetically produced pigments, with the earliest reference being from Theophrastus in the 4th century B.C. [10] and is made by exposing lead to ethanoic acid in the presence of carbon dioxide [11].

The choice of whole egg tempera as a binding medium for the paint was made since it is one of the media used for early Italian panel paintings [11–14]. Any study that improves knowledge of the egg tempera paint system can be considered to be useful for the future conservation of paintings. Furthermore, egg tempera presents a wide variety of chemical compounds and compound classes for study, as shown in a recent review [15].

The aim of this paper is to use DSC to investigate changes in prepared lead white tempera paint films that are subjected to a regime of controlled artificial light ageing, as for the smalt tempera samples discussed in the preceding paper, and then to compare the results to those seen in similar samples exposed to natural ageing in a range of museum and gallery locations.

2. Experimental

2.1. Materials

Basic lead(II) carbonate (Aldrich) was selected in preference to the commercial product sold as lead white by artists' suppliers since it is has a well-known stoichiometry $2PbCO_3{\cdot}Pb(OH)_2$ and its thermal stability has been previously studied in both reactive and inert atmospheres [1]. The binding medium was whole egg as mentioned above and preparation followed a recipe reported in *Il libro dell'arte* by Cennino Cennini [16], as discussed in the previous papers. The preparation was painted onto a sheet of Melinex® (polyethylene terephthalate), which was selected as the support for the tempera, as it is light in weight, allows easy handling and it has shown a high degree of thermal stability [17].

The paint on its substrate was then allowed to cure for a period of 3 months before it was subjected to artificial ageing or field site exposure. This corresponds to the mature stage of the paint and represents the starting point of the investigations in this paper.

Several paint films were prepared containing different pigment and medium concentrations in order to study the modifying effect of basic lead carbonate on the thermal stability of the paint medium and to test how the pigment to medium ratio affected the characteristics of the thermooxidative degradation curve obtained by DSC. The medium content was determined by thermogravimetry (TGA) where the weight losses of (1) pigment and medium, (2) pigment alone and (3) medium alone over the same measured temperature range were recorded. Of these films, medium lean films containing 96 wt.% pigment and 4 wt.% medium were used for the artificial and natural ageing experiments.

2.2. Artificial and natural ageing

Conditions for artificial ageing as discussed in preceding papers involved enhanced light levels,

Fig. 2. Location of the ERA dosimeter in the Clore Gallery.

temperature and exposure to pollutants [18]. Natural ageing involved the exposure of a prepared dosimeter consisting of a number of tempera strips as described in Fig. 1 of [18] (this issue) at six selected sites. Environmental conditions at these sites are given in the previous paper in this issue on smalt tempera.

Two of the locations, however, will be described in detail in this paper. The first of these is Sandham Memorial Chapel in Burghclere, Hampshire, which contains a set of paintings by the British artist, Stanley Spencer. The dosimeter was placed to the upper left of the painting ''Sorting and Moving Kit-Bags'' on the north-east facing wall. At this location the test painting or dosimeter, just like the painting on display, 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. Results on fading tests conducted on ISO standard blue wool samples (used for estimating light damage) that were exposed in the Chapel alongside the tempera dosimeters indicated a total light exposure equivalent to the 9 months exposure period [19].

The dosimeter at the Tate Gallery (Tate Britain), London, was exposed in Room 103 of the Clore Gallery (Fig. 2). This is a newly built extension, which was officially opened in 1987 and houses the works of the 19th century British artist J.M.W. Turner. The number of visitors to the Clore Gallery during exposure of the sensor was estimated to be 190,000. Lighting is provided by a combination of low-UV fluorescent tubes and filtered daylight. During opening hours the illumination is at a constant level of 200 lux. The lighting is switched off when the museum is closed. The Clore Gallery is also air-conditioned with controlled relative humidity and temperature, and 85% air recirculation. Temperature variations were small, between 19 and 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 No. 1), and through activated carbon filters (TR 70).

2.3. Experimental

For DSC measurements, samples (1.5–2.5 mg) were placed into the microaluminium crucibles (3.5 mm OD), which had been especially designed for this project, and weighed on an electronic Sartorius microbalance. A Shimadzu DSC-50 differential scanning calorimeter was used from room temperature to

500°C at a heating rate of 10°C/min and a flow rate of O_2 purge gas of 20 cm^3/min. Oxygen was selected as a purge gas in preference to nitrogen in order to maximise the response from the medium lean samples. Samples were measured in triplicate. TGA measurements were made in order to calculate the pigment to medium ratio of the samples, using a Shimadzu TGA-50, under the same conditions as above but with an O_2 flow rate of 60 cm^3/min.

Infrared spectroscopy was performed on the samples using a Perkin-Elmer FTIR 2000 with TGS detector and 4 cm^{-1} resolution, from 4000 to 450 cm^{-1}. The samples were examined in a Spectra-tech diamond cell with beam condenser giving an effective spot size of 1.8 mm^2, which enabled very small samples to be examined (i.e. <1 mm^2). The instrument cell compartment was purged with N_2 gas to minimise water vapour and carbon dioxide interference and an initial background spectrum was obtained.

3. Results

3.1. Effect of varying pigment content

Fig. 3 shows the DSC curves of lead white tempera control samples that were prepared using different pigment to binding medium ratios. Also shown are the curves for the pure pigment and pure tempera binding medium run under the same conditions. It can be seen in curve (a) that the binding medium has an onset temperature of 190°C and peak maximum temperature of 315°C. In the pigmented tempera sample with 60 wt.% pigment (curve (b)), the main exothermic feature from the decomposition of the medium has a lower peak temperature of 265°C and is followed by a small endothermic peak at 317°C from the decomposition of the basic lead carbonate pigment.

A comparison of the tempera DSC curves in Fig. 3 shows that as the proportion of the pigment in the sample increases, the intensity of the exothermic peak decreases, confirming that it is due to the decomposition of the binding medium. In contrast, the features due to the decomposition of the pigment become more clearly defined as marked in the figure. The comparison of the DSC curves also show that the presence of increasing amount of pigment in the tempera reduces the thermal stability of the medium, as can be seen from the reduction in the peak temperature of the first exothermic peak from 315°C in the pure medium to 265°C in the 60 wt.% pigment sample, to 258°C in the 96 wt.% pigment sample. Furthermore, the presence of the binding medium in turn increases the thermal stability of the pigment, as can be seen from curves (d) and (e). This provides evidence for a degree of pigment–binder interaction.

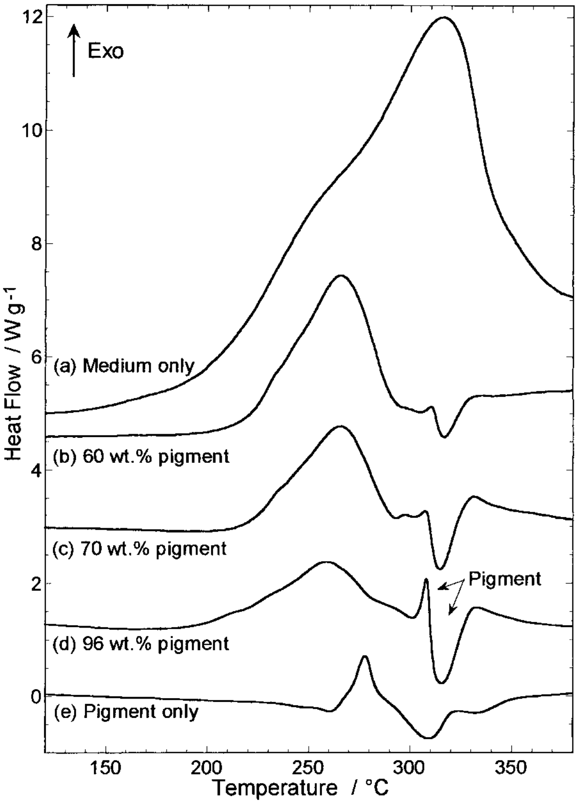

Fig. 3. DSC curves for unaged lead white tempera, showing the effects of different pigment and medium contents. Curves have been vertically offset for clarity.

In the pure pigment [curve (e)] the main changes occur in the 250–350°C region and result from the complex decomposition of $2PbCO_3{\cdot}Pb(OH)_2$ to tetragonal PbO (litharge-dull orange) [1]. The initial exothermic peak (peak maximum 278°C) could be due to the oxidation of some of the intermediate gaseous products that are evolved during the decomposition, possibly CO as observed during the oxidative decomposition of calcium oxalate [20]. In an inert atmosphere this peak is absent and the DSC curve shows only endothermic processes [1]. On further heating in oxygen the tetragonal PbO is oxidised to form Pb_3O_4 (red lead). Evidence for this could be seen in a weak endothermic feature with onset temperature of 420°C. With continued heating to 625°C the Pb_3O_4 would sharply lose oxygen to form orthorhombic PbO (massicot) [1].

The effects of different pigment to medium concentration on the FTIR spectrum of the tempera paint can be seen in Fig. 4. In the 60 wt.% sample the peaks for the pigment can be seen at 3535 cm^{-1} (sharp hydroxyl stretching vibration) and then at 682 and 692 cm^{-1} (CO_3 rocking deformations), and the CO_3 stretching vibration at 1405 cm^{-1} [21]. With even more pigment these peaks appear quite clearly at the expense of those for the medium. Given the high pigment content only the amide I C–O stretch at 1654 cm^{-1} (proteinaceous component) and the ester carbonyl at 1740 cm^{-1} (lipid component) of the egg together with weak C–H stretching peaks at 2950 cm^{-1} and 2850 cm^{-1} are visible. In the papers in this issue on paint tempera it is the changes in the lipid component of the egg which are studied (e.g. mass spectrometry and dynamic mechanical thermal analysis). Therefore the changes in ageing from the infrared data will be described in terms of the change in the shape of the carbonyl peak.

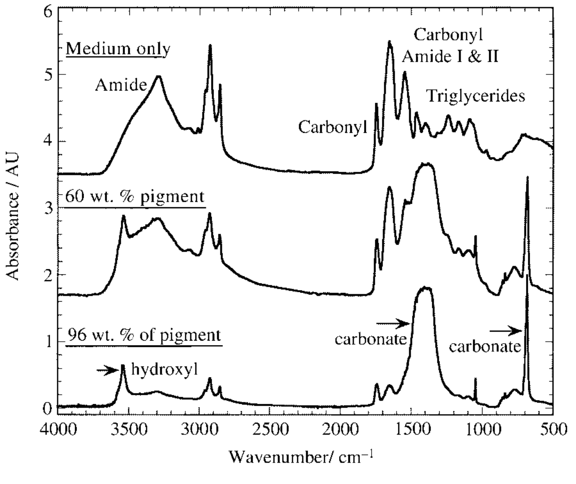

Fig. 4. FTIR data for unaged lead white tempera showing the effects of different pigment and medium contents.

3.2. Effect of light ageing: partial area calculation

Light ageing, as in the case of the smalt tempera, promotes the evolution of a shoulder feature on the leading edge of the DSC curve. The changes are not obvious from a simple visual inspection of the curves, but a systematic trend is seen on more detailed analysis. The evolution of this shoulder feature corresponds to the formation of less thermally stable compounds which degrade at lower onset temperatures than the unaged medium, and has been linked by means of the DTMS results to the formation of oxidation products of cholesterol and glycerolipids, together with the hydrolysis of glycerol esters and the enhanced formation of free fatty acids and dicarboxylic acids (see paper by O. van den Brink [18], in this issue). The presence of more thermally stable lead soaps (reaction between the Pb^{++} and the free fatty acids) occurs in a higher temperature region of the DSC curve, with the growth of a feature between 280 and 300°C.

The area of the DSC curve between 180 and 220°C was calculated as a fraction of the total area taken between 180 and 300°C to give the amount converted within the selected temperature range. Fig. 5 shows the result of plotting this partial area against the days of light ageing. The data reveal that a gradual increase

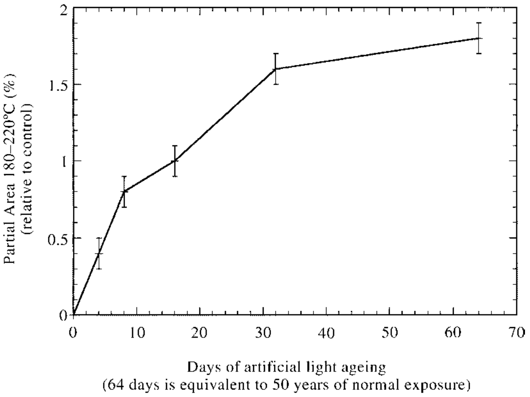

Fig. 5. The effect of artificial light ageing on the partial area of the lead white tempera DSC curve between 180 and 220°C.

in partial area occurs with an increase in the days of light ageing and this is linked to the evolution of oxidation products. The rate of change decreases after the first 8 days and then more significantly after 32 days where a levelling of the reaction occurs. The two control samples, which were stored in separate locations, gave similar values indicating that the measurements were reliable. The curve in Fig. 5 could be used in principle as a calibration graph to quantify the damage from the received light dosage of the paint tempera dosimeter exposed in museums and galleries.

However, the results from the site exposed dosimeters could not be compared directly with the artificially light aged data on the basis of the partial area calculation. This shift in curve position for the site dosimeters prevented the calculation of partial area over the same temperature range as for the light aged dosimeters. One possible exception to this was the Clore (Tate) Gallery dosimeter (TAT) which showed minimum curve shift. This shift in the DSC curves can be seen in Fig. 6, which compares the DSC curve of the control lead white tempera sample with that of the sample exposed at Sandham Memorial Chapel (SAC). Additional chemical changes take place in the naturally aged lead white tempera dosimeters with the formation of lead soaps (lead stearate and palmitate, also mentioned in the mass spectrometry paper [18] this issue).

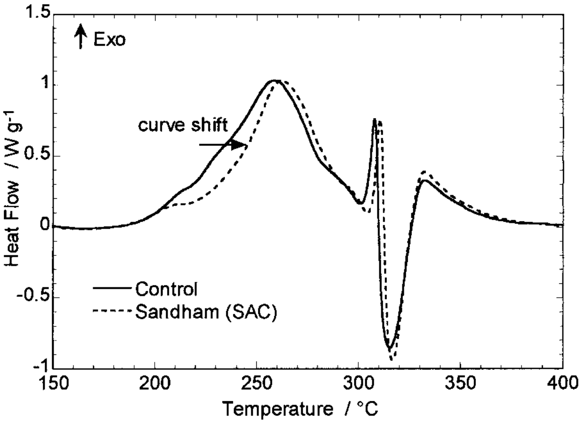

Fig. 6. DSC curves for lead white tempera control sample and sample exposed at SAC, showing the shift in curved position.

3.3. Peak shift calculation

An additional calculation was made which involved the measurement of curve shift of the left-hand side of the main peak at half peak height, as shown in Fig. 6 (expressed as temperature difference relative to the control sample). A plot of peak shift for the site exposed sensors (Fig. 7) is shown, with the artificially light aged samples also shown for comparison. The shift on light ageing is small, being only 3.5°C for the 64 days light aged sample. This is significantly less than that measured in most of the field site exposed

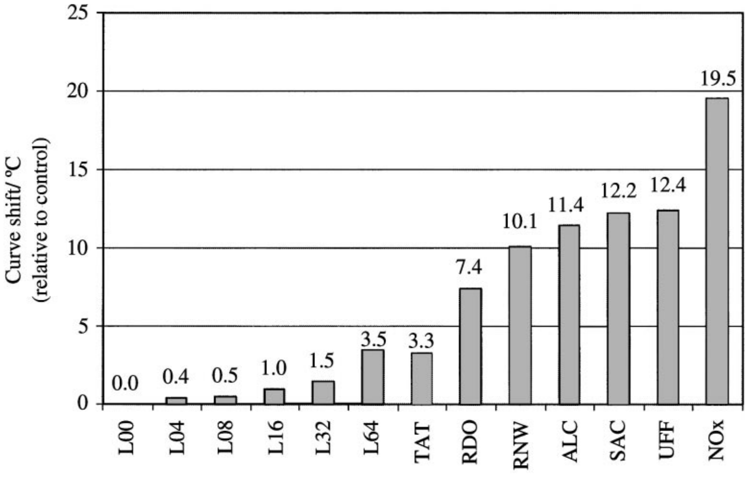

Fig. 7. Thermal stability of lead white tempera samples based on the temperature shift of the main DSC exothermic peak.

dosimeters, where 12.2 and 12.4°C shifts were seen in the SAC and Uffizi Gallery (UFF) dosimeters, respectively. Fig. 7 also shows the strong response from the NO_x/SO_2 exposed lead white tempera. The effect of pollutant ageing appears to promote the curve shift and this occurs almost at 20°C. In this case the effect of pollutant exposure dominates the curve shift. The light ageing effects on the basis of this calculation are negligible.

It appears that the lead white dosimeter in controlled environments does not undergo the significant curve shift, e.g. TAT dosimeter is located between 32 and 64 days artificial ageing. However, as soon as it is placed in unfiltered environments it becomes a very sensitive detector of NO_x/SO_2 levels and generally the presence of pollutants. These are on the whole acidic and will interact well with the basic nature of the pigment. Hence, even RDO shows a response higher than TAT because of the level of pollutants present.

3.4. FTIR analysis

Analysis focused on changes seen in the region of the carbonyl peak at 1740 cm^{-1}. Broadening was seen together with the growth of new features on the low wavenumber side of the peak. Previous work on naturally aged unpigmented egg yolk reported the presence of new features at 1776, 1734 and 1714 cm^{-1} and this was attributed to the oxidation of the triglycerides in aged egg [21]. Changes were quantified by measurement of the carbonyl peak width at three quarters peak height. The width (in wavenumbers, cm^{-1}) of the carbonyl peak was divided by the width of the control carbonyl peak to give a percentage broadening.

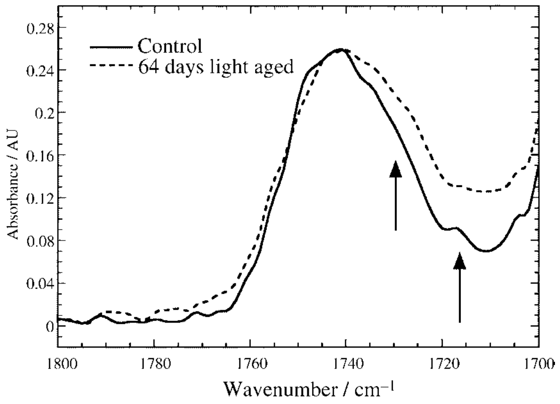

Fig. 8. Effects of ageing on carbonyl peak of lead white tempera.

It can be seen from Figs. 8 and 9 that there is an increased peak broadening with light ageing, but that the changes seen in all the site exposed dosimeters, with the exception of the one exposed in the Clore Gallery (TAT), are significantly greater than those seen in the artificially aged samples. It can also be seen that the effect of NO_x/SO_2 exposure is small, in contrast to that measured by DSC. The low NO_x/SO_2 sensitivity is also seen by mass spectrometry [18], which confirms that FTIR is biased towards changes in the lipid component of the medium like mass spectrometry, whereas the DSC curve is also influenced by pigment effects.

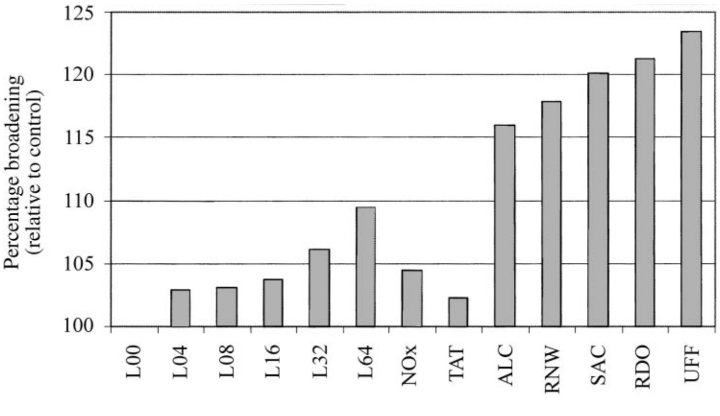

Fig. 9. Broadening of the carbonyl peak in the FTIR spectra of the artificially and naturally aged lead white tempera samples.

4. Conclusion

DSC has been used to investigate the modifying effects of basic lead carbonate pigment on the thermal stability of tempera binding medium, and to study the changes that occur on both natural and artificial ageing. Unlike the smalt, lead white is a reactive pigment. The pigment medium interaction promotes formation of lead soaps. The latter dominates during long term natural ageing (9 months) compared to the relatively short term but more intensive accelerated light ageing. On account of the pigment reactivity and the DSC curve shift a more detailed analysis was eventually required which included discriminant analysis of DSC data. This will be reported elsewhere. In conclusion the effects of natural ageing exceed these of artificial ageing, and those dosimeters at sites where environmental are not controlled (eq Sandham Memorial Chapel) are more affected than those which are controlled (e.g. Clore Gallery).

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