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Issues Relating to Colour Fading in Straw Marquetry

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This paper wishes to explore issues related to colour fading on 'straw marquetry' items. Straw marquetry is normally any object (frequently furniture, small ornaments or pictures) that has been embellished with dyed straw. These decorations range from simple geometric patterns to complex visual landscapes. Straw crafts were widely practised in Europe and have a history dating back to at least the Roman period if not before. Although straw crafts have a long tradition the earliest example of the use of dyes with straw appears to have been in the sixteenth century.

There are few surviving straw marquetry items dating to before the 16th century and the majority of the marquetry collections that exist in Britain were made in the early 18th century by French and Dutch craftsmen that were held in Britain as Napoleonic prisoners-of-war. The main focus of this paper will be light fading issues related to marquetry items made by prisoners-of-war.

The straw marquetry items that were produced by the prisoners-of-war have not preserved well over time, in comparison to those produced by other craftsmen, and the majority has suffered structural damage as well as loss of colouration. This can be the consequence of the limitations imposed by prison life, such as the use of poor quality materials and inappropriate dying processes. It is likely that the dyes used in the camps were possibly more unstable than those used in traditional dyeing methods and may have been more vulnerable towards light damage.

Although synthetic dyes were first produced in 1771 it was only in 1856 that the first synthetic dyes were manufactured and used for practical dyeing. Hence, it is safe to suggest that during the Napoleonic period (1799-1814) that all dyes available to the internees came from natural dye sources. It is also safe to suggest that the colours used in the majority of straw marquetry items that were produced before 1856 were produced by natural dyes.

Although natural dyes were used there are differences between the various colours when they are exposed to light. Some colours appear to survive better than others, although they are displayed in the same environment. Perhaps this is a consequence of different dying processes, or it may simply be that there are differences in the strengths of the different dyes used. Not all the dyes that the prisoners used were new colours that had been extracted from raw materials. Some dyes were actually second-hand or reused. Prisoners frequently extracted the colours from their uniforms and bedding materials. It is quite possible that the observed light fastening differences are a result of this practice.

This paper represents an early stage of research into the conservation of straw marquetry and this particular paper will discuss the causes of fading of dyes. This study will also highlight the possibilities of future experimentation on colour fading of dyed straw items.

Further research on this topic will help the preservation of dyed straw marquetry objects for the future.

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The GCI Lighting for Old Master Drawings Project – an Overview

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ABSTRACT

Paper conservators, scientists and display lighting designers gathered at the Getty Conservation Institute (GCI) in 2002 to consider the challenge of improving lighting for exhibit of Old Master Drawings. After reviewing the history of display of these artworks and the current state of understanding of photo-induced paper and media degradations, participants suggested various approaches to lighting modification. They discussed many areas that would benefit from further research, and recommended particular topics be given a high priority for study. The GCI has continued the project by supporting investigations on several fronts. A summary of the symposium findings and current research and design studies is presented here.

1. 2002 SYMPOSIUM

In autumn 2002, spurred by an enquiry as to whether the length of display of Old Master Drawings and/or the lighting levels in galleries could be raised to improve visitor satisfaction without increasing the risk to these valuable artworks, the Getty Conservation Institute hosted a two-day symposium on this topic. Experts in paper conservation, conservation research, chemistry, physics, and lighting design (Table 1) presented background information in their areas of expertise, discussed the current state of knowledge in this field, and proposed research topics to provide answers.

To start the discussion, historic display conditions for Old Master Drawings (OMD) and the reasoning behind current lighting practices were reviewed. Then the effects of light on the paper supports as well as on the media of the drawings were addressed. It was the general consensus that although in particular instances the structural integrity of the support will be of primary concern, effects of light on the appearance of paper and media are more likely to be at issue.

Cellulose oxidation results in both chemical changes to the carbohydrate monomer units and physical change in the degree of polymerization. Formation of carbonyl and carboxyl groups, cross-linking, and hydrolytic chain scission are all well-documented in pure cellulose and experimental paper samples. Some factors contributing to light damage in OMD are less well understood. The role of other paper components, especially of degradation products already present in old papers, has not been adequately addressed. Relationships between degradation processes and the loss of performance properties of old supports are not well defined.

Studies of media photo-degradation have with few exceptions been phenomenological. Action spectra for degradation ("damage spectra") are generally not available for previously aged, mixed media samples. Mechanisms and rates of post-irradiation changes and the ultimate limits of photo-induced degradation processes have not been determined for many materials in OMD. Evaluations of new lighting technologies must include investigation of their impact on paper and media aging, using historic or suitably pre-aged samples.

Studies of potential modifications to traditional gallery lighting were also reported. The goal of these approaches is to reduce irradiance without the loss of illuminance, that is, to preferentially remove those wavelengths of light that do not significantly contribute to the appearance of the objects. The modifications discussed were based on the work of Thornton (1975) who was first to suggest that it should be possible to achieve good color rendering with a light source consisting of three broad bands in the visible.

In one investigation performed in a divided gallery setting, observers compared the appearance of a print reproduction illuminated with either an MR-16 tungsten halogen gallery light or a set of lamps filtered to provide red, green and blue band light, to a duplicate print illuminated with an MR-16 lamp at a fixed light level (Cuttle, 2000). The participants could adjust the illuminance in the 'test gallery' and also ranked the appearances of the prints using several criteria. Although differences were noted, the three-band 'source' was not found to provide a less satisfactory appearance overall. More importantly, the irradiances at a given illuminance were significantly lower for the three band set-up.

The basis for this can be seen in Figure 1, which compares the output of a hypothetical three-band source with that of an incandescent source. These results provide impetus to the search for practical means of reducing the irradiance of gallery light sources without significantly decreasing illuminance.

Use of filters to remove bands centered at particular wavelengths from a light source was also considered. Results of a pilot study using a specially manufactured dichroic filter to achieve this type of spectrum modification were presented. The results indicated that design of filters to specifications suitable for the palettes of Old Master Drawings should be feasible.

Two other contemporary lighting technologies - fiber optics and light emitting diodes (LED) - were also discussed. These technologies offer the inherent advantage of eliminating ultraviolet and infrared wavelengths. Fiber optic lighting has successfully been incorporated into original lighting fixtures in historic buildings and into exhibition display cases. The light source can be distanced from the display case by a few meters, to avoid heating. At the time of the symposium LED technology, although showing great promise, was not sufficiently advanced to be considered directly adaptable to exhibition lighting

An example of the efficacy of eliminating oxygen, an essential component of photo-oxidation reactions, was also presented. When packets of oxygen scavenger were sealed in a prototype frame with modern materials such as newsprint, the appearance changes that were caused by long-term exposure to daylight in sealed frames without the scavenger did not occur. Removal of oxygen is appropriate only for substances that undergo photo-oxidation. It has the potential to increase damage to materials that are altered by photo-reductive reactions (e.g., Arney, et al., 1979; Giles, et al., 1956). Data on the sensitivities of Old Master Drawing components to photo-induced reduction is scanty. One example is historic Prussian blue, which is well known for its decolorizing tendencies (Berrie, 1997) and which fades in light at low oxygen concentrations. Very low oxygen partial pressure may be adequate to promote oxidation reactions (Thomson, 1986). Research on this topic is needed.

2. CURRENT ACTIVITIES

A lively discussion followed the presentations and resulted in a recommended agenda of further research and technological studies. Several investigators are currently addressing the information gaps that were identified. Adaptation of contemporary lighting and filter technologies is being pursued. Funding not only from the Getty but also from other foundations such as the Leverhulme Trust in the United Kingdom, and the continuing participation of many symposium attendees, make the following projects possible.

Two different approaches to the design of filters for altering the spectral energy distribution of incandescent light sources have been taken. One employs the stacking of color glass filters to create the modified, three-band spectral distribution. The other is a refinement of the multi-layered dichroic filter presented to the symposium. Many layers of thin film dielectric coatings are built up on a glass support. In combination they reject those parts of the visible spectrum that have been deemed more damaging to the components of OMD. The benefits of the former approach are relatively low cost and off-the-shelf availability. The dichroic filters should provide higher efficiencies and less non-specific light loss due to surface reflections.

A key element of both design techniques is optimization of the color rendering index (CRI) for the modified spectral energy distribution. The latter is chosen initially to reduce or eliminate wavelengths most harmful to the materials in OMD and/or least useful to human perception. The CRI is calculated and iterative processes are then used in both approaches to achieve optimization. In addition a theoretical study is being performed to explore the trade-offs between color rendering and the radiant luminous efficacy (lumens/watt) of light sources with continuous and three-band spectral energy distributions. This research is also expected to provide data for design of tests to assess viewer lighting preferences in a gallery-like setting.

Ideally, the shape of a modified spectral energy distribution would be based on knowledge of the action spectra for light-induced damage to the media and supports of OMD, in their current conditions. In the absence of these data, Kubelka-Munk transforms of reflection spectra will be used to approximate the information. It is recognized that absorbed light does not inevitably lead to appearance changes, but in

the absence of photo-degradation studies on aged drawings themselves, absorption spectra provide a reasonable approximation. It is desirable eventually to create a large library of action or absorption spectra of historic and modern drawing materials in their current condition. The initial choice of using OMD has been made in part because of the somewhat restricted palettes found in these works of art.

The development of LED technology has progressed rapidly since the autumn of 2002. The spectra of white LED's have been improved to the extent that these sources are currently used to illuminate dolls in display cases at the Shelburne Museum (Kerschner, 2004). These particular LED's are suitable because the manufacturer does not over-drive them to maximize output, and case heating is not a problem. Two additional LED advances are the development of many more color options and very compact LED's that do not show colored fringes at normal viewing distances. This latter potential problem might be addressed by use of a diffuser, which should also improve overall lighting evenness. The rapid improvements in light quality and stability of these sources have encouraged another participant in the OMD project to begin investigation of their application as an alternative three-band source for lighting OMD (Saunders, 2004).

Development of the sealed package for anoxic display continues, with selection of components that will make the frame less cumbersome and assembly more rapid, and quantitative assessment of effectiveness. A comprehensive investigation of the sensitivity of materials in OMD to photo-induced alterations in the absence of oxygen is slated for the near future. The results of this research and availability of an easily assembled anoxic package should enable widespread use of this means of decreasing photo-oxidative degradation in appropriately chosen OMD.

A test gallery is being planned on site at the Getty, where prototype filters and other new lighting technologies will be evaluated in carefully controlled, blind studies. Color rendering will be assessed, and space will be allotted for aging studies of paper and media samples. But most importantly, measurements will be made to ensure that the newly developed light sources meet the goal of reducing irradiance without significant loss of illuminance.

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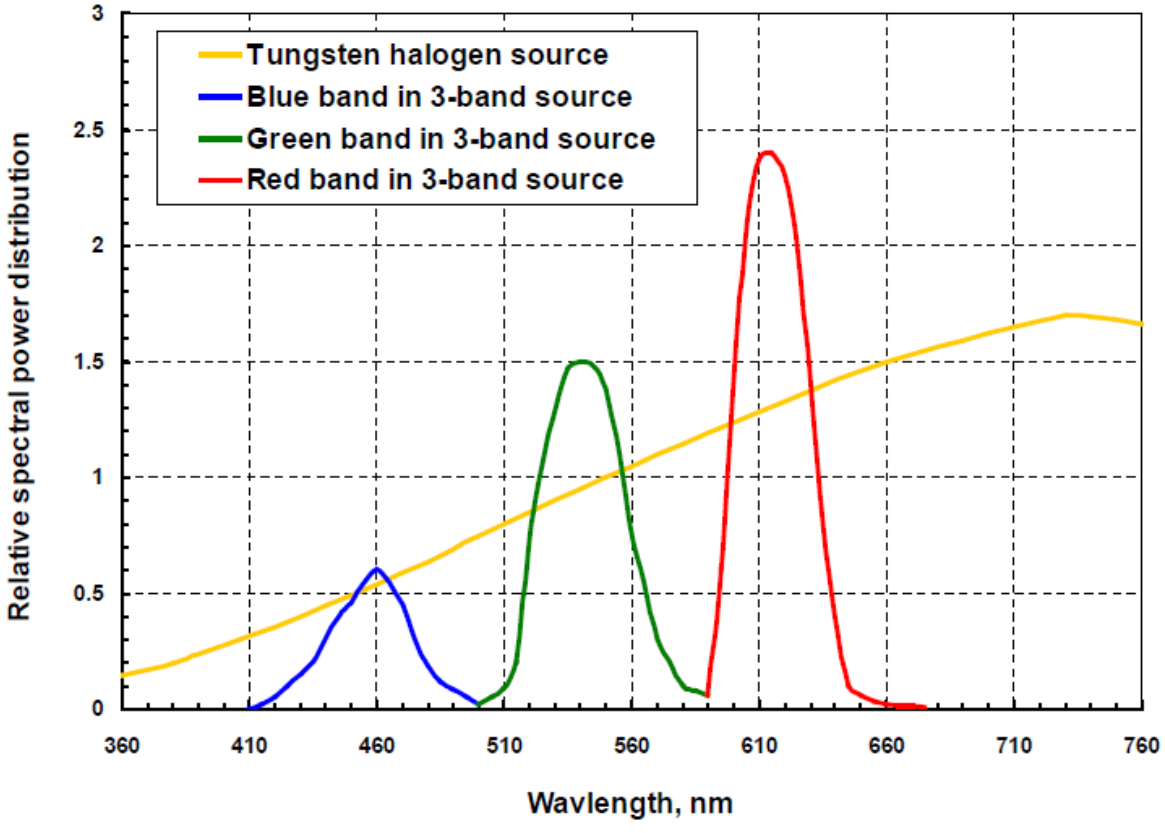
Table 1. 2002 Symposium Participants * Participants continuing, directly or in an advisory position, to participate in research projects.

Christopher Cuttle*	Stephen Hackney*	Terry Schaeffer*
Carl Dirk*	Marc Harnly*	Jean Tetreault
Jim Druzik*	Lee Hendrix	Jeanne-Marie Teutonico
Margaret Holben Ellis	Stefan Michalski*	Piers Townshend*
Christopher Foote	Jack Miller	Nancy Turner*
Mark Gilberg	Arthur Ragauskas	Paul Whitmore*
William Griswold	David Saunders*	Nancy Yocco*

Figure 1.


Tungsten halogen source
Blue band in 3-band source
Green band in 3-band source
Red band in 3-band source
Relative spectral power distribution
Wavlength, nm
0
0.5
1
1.5
2
2.5
3
360
410
460
510
560
610
660
710
760

LightCheck®, new systems for monitoring lighting conditions in museums

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ABSTRACT

Blue Wool Standards (BWS) have been used for years as a cumulative system to monitor light during exposure of museum artifacts. However BWS are not responsive enough for low luminous exposures currently used to exhibit very sensitive artifacts. As an alternative, two new systems, LightCheck® Sensitive (LCS) and LightCheck® Ultra (LCU) have been developed within the frame of an interdisciplinary European Commission project. By readily responding to low luminous exposures, below the detection level of the BWS No.1, these indicators are innovative tools especially designed for a preventive assessment of the risk of damage for light-sensitive objects on display. They consist of a photosensitive dyes/polymer coating applied on an inert substrate. They undergo progressive color variation with increasing luminous exposure, their response to light is cumulative. A fundamental achievement of the research consisted in the definition of the actual respective operative range of the indicators. A calibration of the systems was carried out, and characteristic color-steps easily distinguishable to the naked eye were selected to build a color reference scale. By simple visual examination against this color reference chart, the indicators can be used for an initial, instrumentation-free, easy and fast estimation of the luminous exposure that an object receives in a given environment during a given period.

1. EXPERIMENTAL AND METHODOLOGY

Two main approaches were used for the characterization of LightCheck systems. Firstly, the colorimetric analysis, in the CIE*Lab76 Color System (D65 standard illuminant, 10° Standard observer), provided a quantitative assessment of the light-induced color change. The different responses to light exposure of the samples were evaluated in terms of the color change (ΔE) occurred with respect to the unaged stage. The

second approach focused on the spectral feature evolution, in order to obtain information on the light-sensitivity of the indicators (rate of fading), and on the characteristic light-doses threshold values defining the operative ranges for each prototype. To this purpose, a common protocol of investigation was established, which included non-invasive reflectance spectroscopy in the 350 – 860 nm range (1 nm step). Spectra were collected both before and after different aging treatments. A double beam spectrophotometer Perkin-Elmer λ19, equipped with a 60 mm integrating sphere (8°/D geometrical configuration) was used (resolution ±0.2 nm in the UV-Vis range). The specular component of the signal was excluded.

Samples were exposed at high illuminance (20,000 - 190,000 lux) in light-aging chambers (xenon arc or metal-halide lamp source), with adjustable temperature and humidity. Exposures to fluorescent and natural light sources were also included. Based on these aging experiments, the influence of the lighting conditions was examined (type of lamp, intensity, spectral distribution of the emitted radiation). Exposures at low to moderate intensity levels (100 -700 lux) using tungsten-halogen light bulbs were carried out in parallel in order to simulate conditions closer to museum illuminance levels. Campaigns of on-site exposures of the indicators in selected museums were also performed, specifically designed to investigate the different responses of LCU, LCS and BWS No.1, when used simultaneously in various practical situations. For each experiment, the value of the luminous exposure (or “light-dose”), expressed in luxhours, was calculated and related to the color change occurred on the indicators. Apart from irradiance and exposure time, the influence of other environmental parameters on the fading rate such as thermo-hygrometric conditions were also investigated. Typically, the exposures of the indicators, whether in the laboratory or on-site, were accompanied by continuous monitoring of illuminance, temperature and humidity with a data logger.

2. RESULTS

2.1. COLORIMETRIC AND SPECTROSCOPIC CHARACTERIZATION

The indicators clearly responded mainly to the light-dose received. The typical light-induced spectral variations for LCS and LCU are shown in Figure 1 and Figure 2, respectively. For both, the fading evolution shows the progressive reduction of the band intensities - at different rates - as the luminous exposure increases. The absorption band of the blue dye constitutive of LCS is distinctly identified in Figure 1. This band decreases as the luminous exposure increases. Instead,

in Figure 2, two absorption bands are distinguishable, due to the two dyes used in the formulation of the LCU indicator: a red dye (λmax = 520 nm) and a blue dye (λmax = 620 nm). The colorimetric elaboration was used as main comparative tool of the different behavior of the indicators, and allowed to confirm that, in the range of exposures of interest for practical applications, the indicators obeyed the reciprocity principle. According to this principle, longer exposure times at lower intensities should result in the same effect than shorter exposures at higher intensity. The different levels of light-sensitivity were determined for each indicator in terms of color variation and were compared with BSW No.1. As shown in Figure 3, LCU and LCS cover luminous exposures intervals, beyond which a color saturation is reached (plateau), with best working ranges:

LCU: 0 - 100,000 lux hours

LCS: 60,000 - 400,000 lux hours

As a concrete example, it can be considered that in order to obtain a color change ΔE ≈ 10-12, the following values of luminous exposures (D) are needed:

D ≈ 12,000 lux hours for LCU

D ≈ 60,000 lux hours for LCS

D ≈ 250,000 lux hours for BWS No.1

Variations of temperature and humidity were found to have some influence on the color change. For this reason it was avoided to strictly define the new light monitoring systems as dosimeters. The exposures carried out in several museums (Victoria & Albert Museum in London, Uffizi Gallery in Florence, National Museum in Prague, Cognacq-Jay Museum in Paris and the Jewish Museum in Berlin) corroborated the results obtained in the laboratory.

2.2 CALIBRATION OF THE LIGHTCHECK® SYSTEMS

The results obtained with several samples light-aged in controlled conditions, led to the elaboration of a calibration based on the colorimetric analysis. A limited number of color steps, easily distinguishable to the naked eye were selected, representing a given light-aging stage of the indicators (Figure 4). Hence, color reference scales could be built where each color step can be reliably referred to a range of luminous exposures received by the indicator. The visual comparison between a LightCheck® sample exposed in unknown conditions and the closest matching color on the corresponding color chart can be related with the luminous exposure (Table 1 and Table 2).

2.3 HOMOGENEITY IN THE PREPARATION OF THE INDICATORS

A light indicator designed to become a common prevention tool for the assessment of light environment and light damage to cultural heritage artifacts, and be largely used by the art preservation professionals, has to be a robust system - precise, repeatable and reproducible. In order to achieve a system with reliable response to light, great care has to be devoted to its elaboration. The examination of the spectral features within the same batch of indicators and between different batches, aimed to evaluate the intrinsic error on ΔE, proved that for both LCS and LCU, the color appreciation uncertainty was negligible in comparison with the difference between two adjacent color steps of the reference scales.

3. CONCLUSION

LightCheck® systems were developed as an early warning system, providing an assessment of the risk factor related to light in museums. Albeit, within its determined application limits, light is the factor which effect overrides all other climatic effects, it was shown that other parameters such as temperature, humidity and spectral distribution of the light source may have an influence on the color change. Therefore, LightCheck® systems should be considered as "integrating" environmental indicators. The exhaustive work carried out for the elaboration and characterization of LightCheck® indicators led to the definition of their respective field of application, and showed their usefulness to the targeted purpose of preventive conservation in the cultural heritage sector. LCU and LCS can be used in a complementary manner (as schematized in Figure 5). LightCheck® Ultra is especially suitable for the monitoring of very-light sensitive and fugitive objects, usually exhibited under low levels of light (ISO categories 1-3; e.g. color photographs, watercolors, textiles, natural history specimens), or for short exposure periods, while LightCheck® Sensitive is better suited for controlling the lighting of more durable objects (ISO category 3-6; e.g. oil paintings, tempera, polychrome sculptures, bone, ivory) and/or longer exposure time.

The project team

LightCheck® is a product developed within a project partly funded by the European Commission (Key action "The City of Tomorrow and Cultural Heritage", reference EVK4-CT2000-00016). The interdisciplinary project team consisted of partners from museums (V&A, London), local authorities (SUPP, Prague), industry (Kockott UV-Technik, Hanau) and research institutes (CRCDG-CNRS, Paris, IFAC-CNR, Florence and

Fraunhofer ISC, Bronnbach). The marketing is taken over by Particle Technology, UK. The excellence of the project was awarded with the “Pan-European Grand Prix for Innovation” in Monaco in December 2003.

Table 1. Intervals of the luminous exposures values corresponding to the five color steps in the LCU color reference scale.

LCU	Equivalent luminous exposure (*luxhours*)
4U	75 000 - 100 000
3U	45 000 - 75 000
2U	30 000 - 45 000
1U	5 000 - 30 000
0U	0 - 5 000

Table 2. Intervals of the luminous exposures values corresponding to the five color steps in the LCS color reference scale.

LCS	Equivalent luminous exposure (*luxhours*)
4S	above 340 000
3S	200 000 - 340 000
2S	80 000 - 240 000
1S	60 000 - 100 000
0S	below 60 000

Figure 1. LCS artificially light-aged samples under controlled conditions (Light intensity: I= 30,000 lux, T=40°C, RH=55%). Light-induced evolution, Kubelka-Munk reflectance spectra

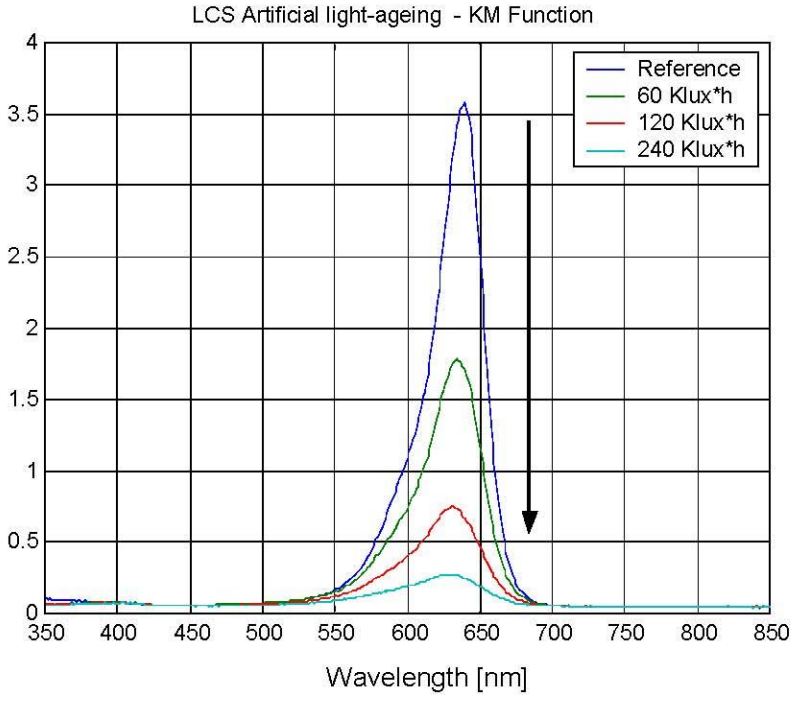

Figure 2. LCU light-aged samples under controlled conditions (Light intensity: I= 100 lux, T=23°C, RH=50%). Light-induced evolution, Kubelka-Munk reflectance spectra.

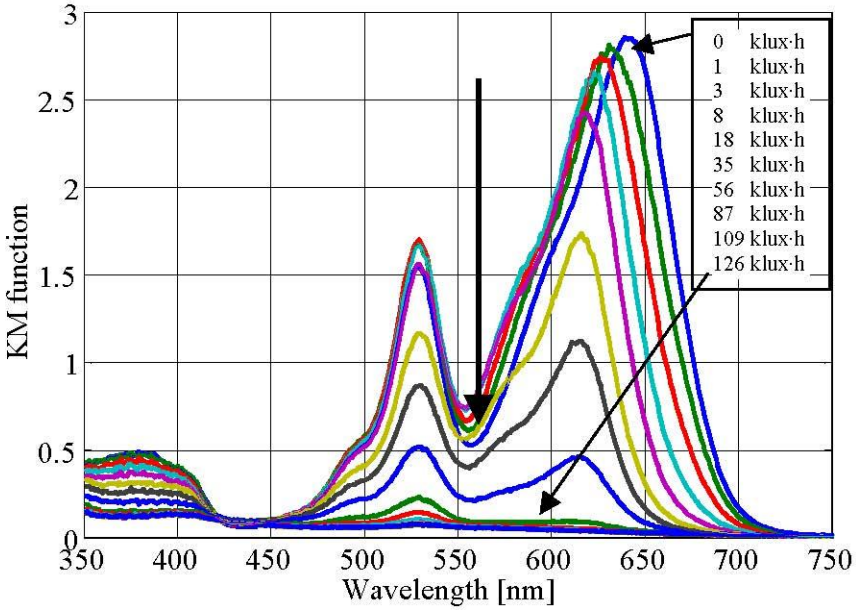

Figure 3. Color change ΔE as a function of the luminous exposure for LCU, LCS and BWS No.1; exposures carried out under controlled conditions (Tungsten halogen lamp, I=500lux, T=23°C, RH=50%).

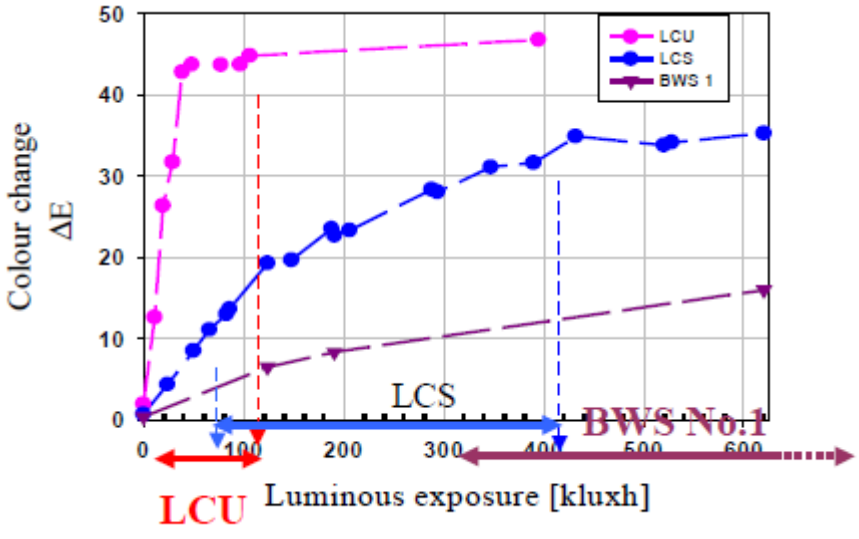

Figure 4. Color reference scale of LCU (left) and LCS (right).

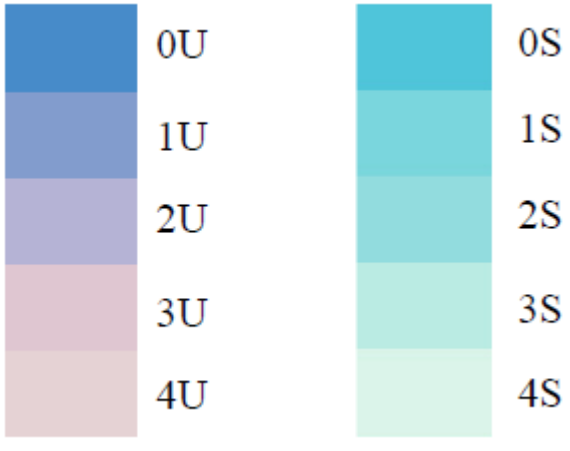

Figure 5. Schematic representation of the range of sensitivity of the LightCheck® systems compared to BWS.

The Identification of Carbohydrates Used by John Singer Sargent for *the Triumph of Religion* Mural Cycle

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ABSTRACT

In 1890, John Singer Sargent started designing a mural cycle entitled *The Triumph of Religion* for the Boston Public Library. A preliminary conservation examination in 1999 detected a carbohydrate-containing surface coating on some of the murals. In 2003, quantitative gas chromatography - mass spectroscopy (GC-MS) was employed to identify the carbohydrates. The GC-MS results indicate the surface coatings contain small quantities of honey, starch and carrageenan. These materials modify the mechanical and optical properties of paint, and were detected on the murals in the central area of the installation space where illumination was effected by skylight. This may suggest Sargent's attempt to balance lighting effects in the installation space.

1. INTRODUCTION

John Singer Sargent's monumental mural cycle, *Triumph of Religion*, is located in the McKim building of the Boston Public Library. In 1893, the library's architectural team of McKim, Mead and White officially contracted Sargent to design a mural cycle for a long and narrow barrel-vaulted hall leading to the library's Special Collections rooms. Three skylights illuminate the central area of the hall, augmented by electric lighting fixtures that illuminate the extreme ends of the hall. This mural cycle depicts a history of Western religion; it comprises 16 mural panels and more than 600 relief elements. The murals were painted in England and then shipped to Boston where Sargent supervised the installation. The murals were installed during four periods: 1895, 1903, 1916 and 1919. The murals have since deteriorated considerably, and their recent restoration is part of a larger renovation of the McKim building.

In 1999, the Straus Center for Conservation at the Harvard University Art Museums surveyed the condition of the murals and conducted a preliminary examination of the artist's materials and techniques. The presence of carbohydrates on some murals' surfaces was detected by staining cross-sections with TTC

(2,3,5 – triphenyltetrazolium chloride). In addition, the surfaces of these murals appeared to have a toning layer that darkened over time; it also contained carbohydrates. During the actual conservation and restoration campaign conducted by the Straus Center in 2003, analysis of cross-sections revealed this surface-toning layer was original. However, it was disfiguring and obscured much detail. The conservation decision was made to reduce, but not completely remove the original coating. Preliminary analysis of the discolored surface coatings using FT-IR was inconclusive but suggested the presence of copal resin and / or cellulose; qualitative gas chromatography - mass spectroscopy (GC-MS) identified drying oils. Therefore, the carbohydrates that were detected by staining cross-sections were analyzed using quantitative GC-MS. The two central questions were: what is the carbohydrate-containing material, and why was it applied?

2. EXPERIMENTAL

Analysis was performed using the Agilent Technologies 6890N Network GC System equipped with the Agilent 5973 Network Mass Selective Detector. The experimental protocol and the databases used to analyze the data were developed at the Getty Conservation Institute (Schilling and Keeney 2003). Sample mass for analysis ranged from 50 to 200 micrograms; remnants from samples removed for cross-sections provided sufficient material. The ten sugars that were analyzed were rhamnose, fucose, arabinose, xylose, mannose and galactose, allose, fructose, glucose, and ribose. Quantitation was conducted using calibration curves ranging from 2ppm to 48ppm; the linear correlation coefficients, r^2, for each sugar calibration curve were greater than 0.995.

The samples were prepared for analysis by first adding 10 µl of a 200 ppm allose solution as an internal standard; this was then evaporated. Next, the samples were hydrolyzed in 100 µl of 1.2 N trifluroacetic acid and heated at 125 ^{o}C for one hour, after being purged with nitrogen for 30 sec. Upon cooling, the solution was removed, evaporated and treated with 80 µl of methoxyamine hydrochloride (100 mg) in pyridine (10 ml) at 70 ^{o}C for ten minutes. After cooling, 40 µl acetic anhydride was added and the solution was again heated for 10 minutes at 70 ^{o}C. Following evaporation at 50 ^{o}C under nitrogen, these sample derivatives were reconstituted in 100µl chloroform.

For GC-MS analysis, 1 µl was injected onto a 30 m DB-Wax column with a film thickness of 0.25 µm and inner diameter of 0.25 mm. Helium was used as the carrier gas at a linear velocity of 60 cm/sec. The splitless injector temperature was set at 240 ^{o}C with a 60 sec purge off time. The mass spectrometer

transfer line was set to 240 °C. The GC oven temperature program was: 105 °C for 1min; 30 °C/min to 180 °C; 5 °C/min to 240 °C; isothermal for six minutes. The solvent delay was 7 min. The MSD source temperature was approximately 200 °C. Single ion monitoring was used.

3. RESULTS

Samples from the murals installed in 1895 and 1903, the first two campaigns, did not show the presence of carbohydrates using the quantitative GC-MS analysis procedures employed in this study. Specifically, these GC-MS analyses included two samples from the mural entitled *Israelites Oppressed*, three from *Frieze of the Prophets*, one from *Dogma of the Redemption*, and one from *Frieze of Angels*. In addition, one sample from *Madonna of Sorrows*, installed in the third campaign in 1916, did not show the presence of carbohydrates using GC-MS analysis. All of these murals are situated at the extreme ends of Sargent Hall where electric lighting fixtures provide illumination. Preliminary FT-IR analyses of the surface coatings on these murals suggest the presence of proteinaceous materials.

The murals in the central area of the hall tested positive for carbohydrates using TTC, and this was confirmed using GC-MS analyses. The total sugar content can be divided into three fractions, namely, the glucose fraction, the fructose fraction and the gum sugar fraction; these data are reported in Table 1. The 'gum sugar' fraction consists of the following six sugars: rhamnose, fucose, arabinose, xylose, mannose and galactose. The distribution of these gum sugars is characteristic for carbohydrate-containing materials, allowing identification of unknown materials. The fructose and glucose fractions are reported separately because the derivatization of fructose is not rigorously quantitative, and the presence of glucose is not restricted to contributions from plant gums. Finally, the surface scraping from Messianic Era, sample K10, was the only sample mass less than 50 µg. The recorded mass for sample K10 was 1.5 µg, but this was so small it may not reflect the actual sample mass that was analyzed.

Table 1. Results from the carbohydrate analysis using quantitative GC-MS applied to samples from *Triumph of Religion* by J. S. Sargent.

MURAL Title	SAMPLE Description	w% all sugars	w% gum sugars	w% glucose	w% fructose
Gog and Magog	Red paint I13	0.133	0.052	0.038	0.041
	Blue paint I12	1.097	0.404	0.330	0.362
	Red paint I17	0.022	0.005	0.008	0.006
Israel and Law	Red paint J17	0.120	0.063	0.026	0.026
Messianic Era	Surface scrape K10	11.690	2.730	4.800	3.900
Heaven	Blue paint N6	0.071	0.006	0.031	0.033
	White paint N4	0.242	0.127	0.570	0.570
Judgment	Darkened drip M1	0.926	0.376	0.296	0.252
Hell	Relief adhesive L2	0.551	0.160	0.192	0.195
Synagogue	Yellow paint O4	0.167	0.053	0.057	0.056
Church	Blue paint P4	0.022	0.012	0.004	0.006
	Red paint P2	0.478	0.144	0.171	0.160

The gum sugar fraction was used to identify the carbohydrate-containing materials that were detected in cross-section using the TTC stain. Identification of an unknown material was based on obtaining a correlation coefficient greater than 0.95, compared to a known material. These data are presented in Table 2; correlation coefficients greater than 0.95, compared to carrageenan, have been right justified

Table 2. Results for the constituent sugars comprising the gum sugar fraction from samples of *Triumph of Religion* that were analyzed using quantitative GC-MS.

Sample	Weight percent 'Gum Sugar' Composition						r^2 to Carrageenan
	Rhamn	Fuco	Arabin	Xyl	Mann	Gal	
I13	0.6	0.5	6.0	9.9	5.4	77.6	0.994
I12	0.3	0.1	3.0	5.8	2.1	88.7	0.999
I17	2.0	4.1	16.3	24.5	8.2	44.9	0.861
J17	5.1	5.8	7.3	8.9	36.2	36.7	0.637
K10	0.4	1.1	5.5	17.2	8.1	67.8	0.974
N6	1.8	0.9	10.8	24.8	9.5	52.3	0.901
N4	0.5	0.2	3.9	29.0	52.9	13.5	0.828
M1	0.1	0.1	0.8	1.3	2.5	95.2	1.000
L2	1.7	0.3	9.7	26.1	42.9	19.3	0.083
O4	0.0	0.0	3.7	12.3	2.3	81.7	0.991
P4	0.8	5.1	10.2	65.3	3.4	15.3	-0.01
P2	0.2	0.2	8.1	20.6	28.9	42.1	0.740
Carrageenan	0.0	0.0	0.0	1.0	0.0	99.0	1.000

The glucose and fructose fractions in the samples that were analyzed may be accounted for by the presence of honey. Analytical results for honey standards are presented in Table 3. Variation in the samples' glucose fraction may be accounted for by the presence of starch. Starch in the paint cross-sections was confirmed by a positive test with iodine. The fructose fraction was expected to have the highest variation using the derivatization procedure that was employed.

Table 3. Standards analyzed using quantitative GC-MS procedures.

Standard	w% all sugars	w% gum sugars	w% glucose	w% fructose
Honey	40	0	38.1	61.8
Honey	56	0	37.0	63.2
Honey	71	0	19.0	81.0
Carrageenan	33	32	0	0

4. DISCUSSION

The results of the quantitative GC-MS analyses indicate that the carbohydrate-containing materials used by Sargent for the Triumph of Religion mural cycle were honey, starch and carrageenan. However, the carbohydrate fractions of the total paint composition are very small. The three samples containing the highest proportions of surface material, specifically samples I12, K10 and M1, contain the highest proportion of carbohydrates.

Starch and honey are well-known artists' materials that are commonly added to oil paints to modify working properties (Gettens and Stout 1966). However, the use of carrageenan as an artists' material is not commonly reported. Carrageenan is a seaweed extract that is used as a colloid stabilizer, for example, to prevent the formation of ice crystals in ice cream. Carrageenan can also be used as a matting agent. The use of this material by Sargent appears to be related to its emulsifying and / or matting properties.

The only existing historical record concerning surface treatments applied by Sargent for *Triumph of Religion* is a letter from the Library Director in 1924, stating the presence of a 'flatting varnish' on the mural entitled *Synagogue*. Interestingly, flatting or 'coach' varnishes are noted as particularly suitable for use with emulsions (Fielding 1846), although exact compositions of these varnishes were closely guarded secrets of coachbuilders and decorators (Wehlte 2001). The primary constituent of this type of extremely hard varnish is copal resin (Field 1850), and the presence of copal was suggested by FT-IR analyses conducted prior to the application of quantitative GC-MS.

5. CONCLUSIONS and FUTURE WORK

The presence of carbohydrates on the surfaces of J. S. Sargent's *Triumph of Religion* murals was initially detected in 1999 using TTC staining of cross-sections. Quantitative GC-MS analyses completed in 2003 identified these carbohydrates as honey, starch and carrageenan. These three materials were only detected in paint samples from murals located in the central area of the installation space where illumination is effected by skylights. Samples that did not contain carbohydrates were from the murals located at the extreme ends of the long, narrow hall where illumination is primarily from electric fixtures.

This has resulted in a working hypothesis that Sargent intended the murals to have a matte appearance in areas where they were exposed to skylight, possibly to reduce glare. In order to test this working hypothesis, the next phase of this examination of J. S. Sargent's *Triumph of Religion* is to apply quantitative GC-MS analyses specific to the detection of proteins and lipids.

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Lightfastness Testing of Artists' Materials Using ASTM D 4303 and the Blue Wools

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ABSTRACT

Conservators are familiar with the use of Blue Wool Textile Fading Cards as exposure monitors in exhibition conditions: they can provide a rough estimate of the amount of light that has fallen on an object. Some conservators have also employed these cards in the performance of ASTM D 5383 and D 5398 lightfastness testing. However, few conservators are aware of the advantages of using ASTM D 4303 as a better set of lightfastness test methods. In this paper, a short history of the development of ASTM D 4303 is presented, and its limitations and advantages are discussed, as are those of using the Blue Wools.

1. INTRODUCTION

Beginning in 1977, ASTM D01.57, Artists' Paints and Related Materials, (a subcommittee of ASTM International, one of the world's largest voluntary standards-writing groups) took the following information into consideration in its development of its lightfastness test methods, first published as ASTM D 4303 (ASTM D 4303) in 1983.

Color change in an art object is initiated by the interaction between the Spectral Power Distribution (SPD) of the light source and the absorption spectra of the colors in the art object. This means that the light source used to test a color used in art must admit all the wavelengths that cause a photochemical effect in a light source that would reach the color, in the most common display conditions. Natural daylight coming through window glass was chosen by ASTM D01.57 to be the primary source for two reasons:

1. It is equivalent to exhibition conditions in the home, in some art galleries and a few museums.
2. It is the traditional exposure used to test art materials for lightfastness since the mid-nineteenth century.

There is ample historical evidence for this choice, and the amount of change that occurs in artists' colorants in oil paints in 200 or more years is fairly well known, based on research published by Robert Feller and Ruth Johnston-Feller (Feller 1975, 1978, 1985). Natural daylight coming through window glass contains ultraviolet light A (UVA), all the visible spectrum, and infrared (IR). UVA and visible light up to about 500 nm (green) trigger color loss––short wavelength light contains more active and energetic photons, and therefore more potentially damaging radiation—, and longer IR wavelengths are known to accelerate color changes.

2. TEST METHOD REQUIREMENTS AND INSTRUMENTATION

In south Florida or Arizona under glass there is 0.5 MJ/m^2 of total radiation per day. Average irradiance on a clear summer day at 340 nm in south Florida is approximately 0.35 W/m^2. Only about 5% of solar radiation is composed of UV, with the remaining 95% nearly evenly divided between visible light and infrared. The percentage of UV to total radiation is lower on a clear day than when thin cirrus clouds or light haze are present, since diffuse skylight conditions enhance the passage of UV spectra.

ASTM D01.57 also considered other conditions:

1. Exposure to cool white fluorescent spectra, also known as "office environment" lighting.
2. Exposure to a combination of window light and cool white fluorescent spectra.
3. Exposure to incandescent irradiance, since that illumination is common in homes, art galleries, and museums.

But in consideration of the total service life exposure of art, D01.57 decided that these conditions were too restricted and less common; and, incandescent illumination causes less color change and is usually only periodic—shorter in duration and intermittent.

We know in addition that humidity and IR strongly affect the lightfastness of a colorant, and contaminants such as ozone gas, ingredients in the vehicle carrying the colorant, or, possibly most important, ingredients in the substrate to which the colorant is applied can initiate color change. However, we decided to eliminate, as much as possible, those conditions from our test methods.

ASTM D01.57 concluded that under glass exposure to natural daylight in south Florida would be the primary illuminant used in evaluating lightfastness of artists' colorants. There are two test sites there,

run by Atlas South Florida Test Service (a division of Atlas Materials Testing Service) and Q-Lab Weathering Research Service (a division of Q-Panel Lab Products), which we use with their generous, voluntary, cooperation. Since we knew that the heat and humid conditions there could cause some colorants to change, even though they had been shown not to do so in home or gallery environments, we also chose a second outdoor location that excluded, as much as possible, humidity. The first site was in Winfield, KS, operated by Liquitex, a manufacturer of artists' paints. Today, we use two test sites in Arizona, again each run by Q-Lab and Atlas. Although we used Atlas exclusively for about the first 10 years of testing, we now use Q-Panel in addition.

In the first set of tests made by Henry Levison (founder of Permanent Pigments, an artists' varnish, medium, and paint-maker), 172 artists' paint specimens applied to an inert substrate were exposed to natural daylight in both south Florida and Winfield, KS; to Verilux brand High Output (HO) fluorescent lamps (no longer manufactured), in an instrument built by Levison (see Annex A1 in ASTM D 4303); and in the test chamber of an Atlas Ci 35, a water-cooled xenon arc exposure instrument equipped with filters to simulate the natural sunlight through window glass. Of these 172 colorants, 10 were controls; that is, we knew the history of color changes documented to take place in them over more than 100 years of indoor exposure. Moreover, the colorants, in this case artists' pigments in standard oil paint vehicle, were reduced with a standard white paint to 40% reflectance at the wavelength of maximum absorption for each particular pigment. Most artists use white in mixing tints of colors, so this was a more accurate reflection of actual use of the material; and, mixing the tint to 40% reflectance at the maximum absorption wavelength ensured that the materials would be exposed to a severe test.

Mr. Levison's exposures at first continued until 50,000 Langleys of irradiation accumulated (A Langley = one calorie/cm^2; one Cal/cm^2 = 4.184 Joules/cm^2, or 41840 J/m^2; 50, 000 Langleys = 299200 J/m^2). But visual examination of the initial specimens following this test showed that 30,000 Langleys, or 1260 MJ/m^2, was the optimum amount of exposure to obtain results that agreed with the changes known to take place in the 10 control colorants. In addition, this reduced exposure did not bleach many of the less lightfast colorants so badly that visual comparisons with the more lightfast colorants was distorted. That is, once a color has bleached there is no more color change with further exposure, while a more lightfast color may continue to change. When bleached completely white, a light color may have lost fewer units of color difference (expressed as CIELAB units using a color difference formula that gives results as "ΔE") than a more lightfast dark color.

ASTM D 4303 therefore originally required two continuous exposures—one under glass to south Florida daylight; and one to properly filtered xenon radiation, or full spectrum HO fluorescent radiation, or, in some cases, to the radiation in an Atlas HPUV (fluorescent) instrument—until 1260 MJ/m^2 was reached. Subsequent problems arose: the specified fluorescent lamps for Levison's homemade instrument went out of production by their manufacturer and no suitable substitute has been found, and at that time no commercial version of the fluorescent exposure apparatus was available—each one had to be custom built by the test operator. One other fluorescent instrument was built by Takahiro Takigawa of Turner Colours (Japan), who also bought the entire remaining stock of Verilux lamps. Now, ASTM D 4303 tests on coloring materials use the natural daylight exposure and the xenon exposure, even though D 4303 still references a fluorescent method.

3. ASTM PERFORMANCE STANDARDS BASED ON D 4303 RESULTS

Based on D 4303, a standard paint specification was written: ASTM D 4302, for artists' oils, alkyds, and resin-oils (ASTM D 4302). When we contemplated writing standard specifications for artists' acrylic dispersion paints, artists' transparent watercolors, and artists' opaque watercolors (gouache paints), we realized that these paints and their substrates might be too sensitive to the RH of the south Florida exposure. Tom Vonderbrink of Permanent Pigments' successor company, Liquitex, established control pigments so that the HPUV instrument from Atlas could be used as an alternate way to test colorants in the standard acrylic dispersion vehicle, a standard watercolor vehicle, and a standard gouache paint vehicle. Thus, we were able to continue to specify two different test methods for lightfastness with a third method available in case anomalous results arose from testing in the two preferred methods, and D01.57 produced D 5098 for artists' acrylic paints, D 5067 for artists' watercolor paints, and D 5724 for artists' gouache paints (ASTM D 5607).

When D01.57 began tackling artists' colored pencils, in about 1994, a new set of problems arose: these are mostly mixed colorant products, as opposed to the mostly single colorant products we had been testing, and they are even more sensitive to the moisture of the south Florida exposures. By this time the Winfield KS site had closed, as Binney & Smith consolidated Liquitex's manufacturing operations in New Jersey, but the new sites in Arizona became available.

Simultaneously, we found around 1999 that results from two new table top xenon instruments, from Atlas and Q-Panel, correlate with the results from the larger xenon arc instruments, and that exposure to natural daylight at the Arizona sites during the winter months would not damage moisture sensitive colorant products (water-soluble colored pencils) or substrates (paper). This has allowed us to offer more choices of exposure to manufacturers of artists' materials, and to reconsider the use of machines requiring HO full spectrum fluorescent lamps or cool white fluorescent lamps, the Q-Panel QUV Accelerated Weathering Tester, and the Atlas HPUV. Considering the continuing difficulties with fluorescent exposures for artists' materials, it is possible that the requirement for them will be dropped from D 4303. Of course, fluorescent exposures are still useful if one wants to test the endurance of materials exposed to "office environment" lighting, but they are not useful to those interested in the longevity of colors used in art. To ensure continued development of correlations between natural and simulated accelerated testing, two different exposures, to natural daylight and to simulated daylight (filtered xenon) will still be required.

4. OTHER METHODS OF EXPOSURE

In contrast to these exposures and measurement methods, other types of artists' colorant-containing images, such as color photographic prints or inkjet printing ink prints, are currently being tested by using lux as the measurement unit. In this method, the photometric quantities are weighted to human visual response, and therefore do not include most of the actinic spectral energy significant in initiating photodegradation, in particular the UV and IR portions of the spectrum. This is possibly because the test method accounts only for the most common type of consumer use of these products: periodic exposure to light. That is, most photographs and digital printed matter are stored by consumers in albums and only looked at occasionally.

Artist's versions of these products, however, are meant to be exhibited more continuously, on walls in homes and galleries, and for longer periods in museums. It is therefore more appropriate to test the exposure resistance of these materials, as used by artists, under the irradiance from the entire visible spectrum, to include both UV and IR radiation, and to use the joule as the measurement unit—the joule can be applied to the entire spectrum and is a well-established unit in international standards.

5. MONITORING IRRADIATION

In Henry Levison's original HO full spectrum fluorescent light apparatus, an Epply pyranometer and a recorder calibrated in Langley units attached to a digital readout meter were used to record and monitor the amount of exposure—at the time, no commercial instrument that could measure spectral irradiance was available. Levison did not realize, apparently, that Langleys are not an appropriate unit for any irradiance measurement except solar and are even discouraged for that use.

Today, spectral radiometers are available that can monitor and record irradiance accumulation. These radiometers are built into xenon exposure instruments, and automatically keep track of the amount of a specific light that is being used to expose specimens. In the natural outdoor exposure racks, spectral radiometers are built into the enclosures and can send measurements to the laboratories for record keeping. These radiometers are themselves required by agreed-upon operating procedures to be recalibrated about every 1000 hours of use by means of a supplied "calibration radiometer" that accompanies the xenon instrument. Independent users of the instruments, such as the author, therefore must send the calibration radiometers to the original manufacturer for recalibration to a standard.

In xenon arc radiation, the light is passed through either a clear Window Glass Filter to force the SPD of the illumination to resemble the full spectrum of natural daylight. This makes a good match for all but the IR portion of radiation in natural daylight. Therefore, to encourage the acceleration of color change promoted by IR, the black panel temperature of the xenon test chamber is monitored at 63°C for the duration of the test.

Several other questions are considered in the exposure methods of D 4303:

1. What is the method of measuring the irradiation produced under the different conditions?
2. How much radiation is required to hit the specimens in the artificial radiation environment to be equivalent to the 1260MJ/m^2 of the natural exposure radiation?
3. In the xenon exposure, what level of irradiation should be set that will accelerate the test but not distort the results?
4. What role does humidity play in the color changes of certain specimen/substrate combinations?

6. MEASURING IRRADIATION AND DETERMINING RADIANT EXPOSURE TIMES

A spectral radiometer can be used to monitor the radiation falling on specimens, as already described, in both artificial and natural lighting test conditions. Some xenon arc instruments can be set to monitor the radiation at one of two set points: 340 nm or 420 nm. Others monitor at a band of wavelengths—either 300-400 nm or 300-800 nm. D01.57 chose to have the monitoring done at 340 nm, to include UV.

Kurt Scott, a scientist at Atlas Electric Devices, in the early 1990s calculated the equivalence of 1260MJ/m^2 of the natural daylight exposure to be 510kJ/m^2 in the Atlas Ci 35, monitored at 340 nm with the irradiance level set at 0.35 W/m^2. The duration of the exposure to reach 510kJ/m^2 was 410.5 hours. This has been the standard specification for the xenon machines, both laboratory size and table top versions, ever since. The instruments are set to end the test when 510kJ/m^2 is reached, not when 410.5 hours is reached, but for estimating lab time, knowing how long the test takes is useful.

This last point is a further refinement of less sophisticated test methods: D 4303 sets an end-point to the test, whereas methods based on lux and some fluorescent exposures do not.

Cool White Fluorescent exposures in instruments like the Atlas HPUV or Q-Panel QUV present a different problem: although the actinic wavelengths are included in the emissions (~375 nm to a peak of ~600nm to ~675 nm), the SPD of the Cool White lamps is not the relatively smooth curve of a xenon lamp or natural daylight, but exhibits the spikes characteristic of fluorescent illumination. Therefore, colorant controls were developed by ASTM D01.57 to be sure that specimens exposed in the fluorescent apparatuses changed in the same way that they did when exposed to the 1260MJ/m^2 of natural daylight to allow the use of these instruments.

The fluorescent UV/condensation test apparatus, for instance, may use three types of lamps: UVA or UVB lamps, or Cool White fluorescent lamps, combined with the option of condensing humidity to reproduce the effects of UV and moisture. The UVA 351 lamp produces UV beginning at about 310 nm and continuing to about 400 nm but does not irradiate between 400 nm and 500 nm, which has been demonstrated by D01.57 and conservation studies to cause color change. However, we know that fluorescent lamps should not be used when the effects of long wavelength radiation are anticipated—that

is, when IR plays a role, fluorescent lamps, even those that include UV, should not be employed in accelerated lightfastness testing.

7. THE BLUE WOOLS

The so-called "Blue Wools" have for more than 25 years been widely used in museums as exposure monitors. That is, a card is put into a vitrine, for example, and used to keep track of the amount of light falling on the enclosed objects. Or, a card may be placed in an inconspicuous location in a museum gallery, to monitor the general accumulation of light exposure in the room.

Three types of Blue Wools monitors are currently available:

1. An experimental paper printed with a blue pigment mixed to be a color equivalent to BW 4 (called Pigmented Paper Light Fastness 4, or PPLF4) [As of this writing, the PPLF4 papers are no longer being produced]
2. Sheets of fine blue wool cloth dyed in the various blue wool steps (i.e. BW 3, 4, 6, 8, and so on)
3. Textile Fading Cards, which each have 8 strips of dyed blue wool with increasing steps of lightfastness, adhered to a paper card: beginning with BW 1, each succeeding step is twice as lightfast as the preceding step.

In experimental data reported in 1978 and 1985, Robert Feller and Ruth Johnston-Feller, long proponents of using the Blue Wools as light monitors in museums, theorized that if a colorant lasted as long as BW 6+, the equivalent museum condition exposures would be more than about 100 years.

In practical use, the Blue Wools are exposed along with the colorant or object in question, and changes in the blue dyes are monitored. In ASTM D 5383 and D 5398 (ASTM D 5383), one half of a Textile Fading Card is covered, as are strips of coloring materials (for instance, paint, ink, markers, colored pencils, and so on). According to the ASTM specifications, a separate card must be used for each test panel, in order to assure that the same radiation is falling on all the samples. This is one reason why kits for performing the tests, such as those sold by Golden Artist Colors (the only producer of such kits known to the author) are of limited size. In his own experiments during the development of these specifications in the early 1980s, the author was able to make panels that held as many as 27 colored samples each; in one round of tests of the method during 1981, about 700 colorants of various sorts—excluding traditional artists' paste paints–were tested this way.

In the 25 years that the author and his colleagues have used the various forms of the Blue Wools, primarily the Textile Fading Cards from Talas, we have noticed several significant problems with them. First, there are two manufacturers of the blue wool cloths: the American Association of Textile Chemists and Colorists in Research Triangle Park, NC, and the British Society of Dyers and Colourists, in London. Each is made differently, although both conform to specifications written by the International Standards Organization (ISO). The AATCC Blue Wools are made from a mixture of two dyes, one stable and one unstable—the amount of each dye controls the rate of fading in the cloths. On the other hand, the BSDC cloths are made of eight different blue dyes, each with its own rate of fading. The author knows of no published studies which correlates the two different brands and their rates of fading—although Joy Turner Luke is working on a study. Second, the fine wool cloth from which the blue wool strips on the Textile Fading Cards are made is apparently bleached before it is dyed blue. When the BW cards are then exposed to natural daylight and begin to fade, the cloths turn perceptibly yellow. We do not know if the bleaching process causes the yellowing, or whether the glue used to attach the strips to the card contributes to it. In either case, during the process of determining visual color change, this yellowing affects the perception of contrast between the exposed and unexposed portion of the BWs, and may therefore significantly affect the reporting of subjectively observed color changes in tested specimens.

Moreover, no conclusive correlation between the results of ASTM D 4303 lightfastness testing and the methods employed in D 5383 and D 5398 has been found. In a recent testing program during 2000-2003, funded by the NCPTT and the Kress Foundation, the author and his colleagues subjected around 350 pastels to two D 5383 tests (one in northern California and one in northern Virginia) and a D

4303 test. In the D 5383 tests, numerous observers, as instructed by the test method, rated the results—all the ratings from each of the two tests were then averaged in an attempt to make the results less subjective. In the D 4303 tests, each sample was read by a colorimeter in four different locations before exposure, and the results were averaged to eliminate some uncertainty about the evenness of the sample preparation; after the xenon exposures, the samples were again read four times and averaged. The ΔEs were calculated from the two averaged readings. In addition, a small selection of samples was tested using a microfadeometer developed at the Center on the Materials of the Artist and Conservator at Carnegie-Mellon University. Even after all this, little correlation among the results was observed.

Until such time as Joy Turner Luke is able to report on her current studies of the Blue Wools, the author concludes at this time that although they are useful for general light exposure monitoring, they should not be used for the scientific examination of color change under accelerated exposure conditions, and must not be used to publish information about the lightfastness of artists' materials. ASTM D 4303 provides a much more accurate and reproducible test method, with a proven history for lightfastness testing of artists' materials.

ACKNOWLEDGEMENTS

I am grateful to my AIC, ASTM, and ISCC colleagues, who since 1978 have provided me with a better education than I ever received in a university. In particular, I want to thank Fred Billmeyer, the late Max Saltzman, the late Ruth Johnston-Feller, Robert Feller, the late Henry Levison, the late Ray Kinmonth, Kurt Scott, Eric Everett, Pat Brennan, Oscar Cordo, Mark Golden, Joy Tuner Luke, Ross Merrill, Jay Krueger, Paul Whitmore, and Roy Berns. I also want to acknowledge with thanks the support of the Samuel H. Kress Foundation and the National Center for Preservation Technology and Training for their continuing interest in lightfastness research.

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The use of lightfastness and other testing protocols in real-life conditions: Devorah Sperber's "Reflections"

Sarah Lowengard, New York City

What happens to an artwork when the combination of materials used and the conditions of display are known and beyond stringent control? This was a situation faced recently by the artist Devorah Sperber. In 2003, she was commissioned by the Public Art Project of Puerto Rico (Proyecto de Arte Público de Puerto Rico) to create an artwork that would include 80,000 spools of thread, for a train station described as "non climate controlled with heat, humidity, salt air, and dust."(Conservation DistList Instance 17:24). Her concerns, and concerns of the commissioners, include not only the lightfastness and longevity properties of the components in an uncontrolled environment, but also the potential effects of a hurricane and other strong weather or natural disasters on the artwork. Two significant parameters seem to pull the project in different directions. A criterion of the project is that all materials, including any substance applied to them, had to meet building codes. The contracted "life" of the artwork is ten years; the blink of an eye for many conservators, and many testing protocols.

The result is an interesting collection of questions for any testing program. Components that range from natural composition and deterioration of plastic spools of cotton covered polyester threads, to the comparative value of applying a UV-blocking substance to the thread and their plastic support. They suggest a need to assess techniques to slow visual or structural deterioration from light and also the potential for damage that a coating –or no coating –might create.

This poster will describe a project-in-process based on the use of a proprietary product, UV-Block (Atsko, Inc, Orangeburg, SC), and the adaptation of standard test protocols to predict behavior and suggest mitigation techniques for a new artwork under the circumstances described. It will begin to address both the artist-conservator collaboration raised here, and questions about why such testing programs are –or, perhaps, aren't –a useful tool in the preservation of art.

Damage Assessment in Historical Parchments and Tapestries: application of thermomechanical and thermoanalytical techniques

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ABSTRACT

This paper will describe how thermomechanical and thermoanalytical techniques have been used to characterise the physicochemical state of (1) wool and silk threads in historical tapestries (project title Monitoring of Damage in Historic Tapestries (MODHT) EV4K-CT-2001-00048, http:\\www.hrp.org.uk) and (2) historical parchments (project title Improved Damage Assessment of Parchment, (IDAP) EVK4-CT-2001-00061, http:\\www.idap-parchment.dk). Both projects are currently funded by the European Commission under the 5th Framework Programme. In both cases model samples have been subjected to accelerated ageing; in the case of tapestries this has involved light, in parchment conditions of elevated relative humidity and temperature have been used as well as light and then combinations of light, heat and NO_2. Model samples of parchment were readily available from suppliers whereas model tapestries had to be specially prepared for the project and this involved weaving and dyeing according to traditional practices. In both cases selected historical samples have been made available; parchment from the sample collections based at the School of Conservation in Copenhagen, and wool and silk threads from tapestries in collections at Hampton Court Palace, the Royal Palace in Madrid, and selected museums in Brussels and Bruges. All the samples have been analysed using a combination of advanced analytical techniques. In this paper the focus will be on the information obtained mainly from thermoanalytical techniques. Dynamic mechanical thermal analysis (DMTA) has been used to measure Young's modulus of woven pieces (and threads) from model tapestries and threads from historical samples, and parchment samples. DMTA allows measurements to be made on relatively small samples (5 mm threads) compared to

the size used by the more widely known industrial tensile tester. DMTA in reverse configuration has been used to measure the shrinkage behaviour of parchment, as in the previous MAP (Microanalysis of Parchment) project (Odlhya 2002). Controlled environment dynamic mechanical thermal analysis has also measured the effect of increasing relative humidity on woven pieces of tapestry (wool) (Foster 2003). Thermal stability indices have been calculated from thermogravimetry for parchment and from differential scanning calorimetry curves for tapestry (silk).

1. INTRODUCTION

The overall objectives of the two research projects discussed in this paper are as follows: for historical parchment the establishment of a parchment damage assessment programme, an early warning system and a digitalised user-friendly parchment damage atlas; for tapestries a better understanding of the materials and techniques used in their construction and the mechanisms of degradation. This is being achieved through the preparation of model tapestries according to traditional techniques, and sampling from historic tapestries in Northern and Southern European locations. In both projects an integrated analytical approach is used to characterise the physicochemical properties. The research projects are coordinated by the School of Conservation, Copenhagen (IDAP parchment / Dr.R.Larsen) and the Textile Conservation Dept at Hampton Court Palace (MODHT tapestry/ David Howell). The contribution described in this paper to both projects focusses on the application of mainly thermomechanical techniques (isothermal and isothermal at controlled RH programme), and thermoanalytical (thermogravimetry and differential scanning calorimetry) techniques. The aim is to record changes with occur on accelerated and natural ageing and identify markers which can provide an assessment of the extent of damage in naturally aged materials.

2. METHODOLOGY

2.1 THERMOMECHANICAL TESTING (DYNAMIC MECHANICAL THERMAL ANALYSIS DMTA)

This was performed using the Rheometric Mark 3 dynamic mechanical analyser (DMTA) under isothermal conditions in reverse configuration. The instrument has several modes of measurement: test which involves application of a static load increasing from 0 to 7 N over a period of 10 min (stress/strain), test where a small static load (0.1 N) is applied and this enables the amount of displacement (or creep) to be measured (creep test). The inverse configuration

allows in situ monitoring of (a) wetting and heating through to 90 °C and was originally used for monitoring shrinkage in parchment (Odlyha 2002) and (b) in situ monitoring under conditions of controlled RH for both parchment and model wool tapestry samples (Foster 2003).

2.1.1 Stress/Strain test

Testing was performed on model woven (wool) tapestry samples. Samples in the form of a rectangular piece (20 mm x 10 mm) were held in the tensile clamp of the DMTA analyser and for historical threads a free length of 5mm was used. Measurements were made along the weft direction, along which the tapestry experiences load on display.

2.1.2 Creep test

2.1.2.1 Immersion in water and heating

Samples were held in the tensile clamp under a low static load (0.1 N) immersed in water and heated 5°C every 10 minutes until 80°C was reached. In all cases shrinkage of the samples occurred. A ratio was calculated based on the main shrinkage to that of the total shrinkage as in the previous MAP (Microanalysis of Parchment) project (Odlyha 2002).

2.1.2.2 Controlled RH environment

A protocol for testing the response of model tapestry samples to variations in RH was established. Samples were dried overnight and then subjected to a humidity ramp (1%/min) from 10 to 80%RH. RH values were selected at which differences were most pronounced and the resulting displacement was measured. For the model woven wool tapestries expansion was followed by a pronounced shrinkage and a ratio of expansion to shrinkage was calculated.

2.2 MICRO-THERMAL ANALYSIS (µTA)

Micro-TA combines the technique of atomic force microscopy (AFM) with thermal analysis to provide spatially resolved information on parameters such as the glass transition temperature or

softening temperature (Pollock 2001, Price 1999). The most common probe used for micro-TA is the Wollaston resistive thermal probe, which is capable of acting both as a temperature sensor and as a heater This enables variations in local thermal conductivity (as well as topography) to be imaged in a lateral spatial resolution at the µm scale (scanning thermal microscopy – SThM) and localised thermal analysis (L-TA) to be carried out, typically on a few μm^3 of material.

2.3 THERMOGRAVIMETRY (TGA)

Thermogravimetry (TGA) monitors the change in mass with temperature or time when a sample is subjected to a linear temperature programme and controlled atmosphere. Conditions identical to those established in the previous MAP project were used to extend the database to include accelerated aged samples. Samples were heated in an oxidising atmosphere at 10°C/min and sample size used was between 1 to 1.5 mg.

2.4 DIFFERENTIAL SCANNING CALORIMETRY

Samples (0.1-0.5 mg) were heated in micro-Al crucibles in an oxidative environment and the enthalpy value of the resulting exothermic peak was measured. This approach had previously been used to characterise binding media in paintings (Ohlyha 1995), and in the tapestry project has been used mainly on the model silk threads from the woven silk tapestries and historical silk samples.

3. SAMPLES

The results reported in this paper are taken from samples tested in the following manner. Accelerated aged parchment samples and naturally aged parchment samples from bindings and manuscripts were obtained from the School of Conservation, Copenhagen. Accelerated ageing of parchment samples involving RH and T (40-80°C and 40-80% RH) was carried out at the School of Conservation, and light, heat and pollutant aged samples were prepared at the Centre de Recherches sur la Conservation des Documents Graphiques (Paris). Pollutant ageing (NO_2) involved exposure between 2-16 weeks at 50 ppm also in combination with heat (100 °C) and light (5.4 Mluxhrs). For the tapestry project model tapestries were woven and dyed in the Department of Textiles (University of Manchester) according to traditional practices. Light ageing of the model wool tapestries was performed in the Textile Conservation department in Hampton Court Palace. Samples were aged for 400 hours in the Xenotest (90 Mega lux

hours). This is approximately equivalent to 400 years exposure under normal museum lighting conditions.

4. RESULTS AND DISCUSSION

4.1 THERMOMECHANICAL TESTING

4.1.1 Stress/strain test:

Model woven tapestry (wool) Figure 1 shows the results obtained from the stress/strain data for model tapestry pieces (20 mm x10 mm) measured by DMTA. Young's modulus values were calculated from the slope of the stress strain curves. The coloured bars correspond to the dye colour: from left to right control, red dyes (madder, cochineal, Brazil wood where "L" indicates the presence of lye), black mordanted wools (alder bark tannin/oak galls) and treated with iron (11) and copper (11) sulphate containing solutions (BLKW4), green (weld/woad), blue (woad) , mordants (alder bark tannin, alum, and oak gall), and yellow (YW2 dyer's greenweed, YW1 weld). Dyeing and mordanting processes in most cases reduce the stiffness of the sample to varying degrees; the most affected were GRW2 (woad/weld dyed), YW1 (weld dyed), and mordant (oak gall). This is in accord with measurements made with larger sample size on the Instron tensile tester (Hallet). In the case of RW2 (madder) the presence of lye reduces the sample stiffness. The madder dyed sample (RW2) which has also undergone two mordanting processes (first with oak galls and then with alum) appears to increase in stiffness. This difference in behaviour is also observed in the response of the same sample to the relative humidity testing shown in Figure 3.

Woollen threads from model woven tapestries and historical tapestries

Young's Modulus values for most of the unaged and light aged undyed and dyed woollen threads (removed from the woven pieces) were found to be within the range 4000-2000 MN/m^2. Samples from three Hampton Court Palace tapestries were examined. The Young's modulus values of most of the historical wool threads from three tapestries were found to lie between 500-1500 MN/m^2. This indicates that significant loss in strength has occurred. Samples were removed from the back of the tapestries so that light cannot be considered as the main damaging factor. Threads from "Triumph of Death over Chastity" c.1500-1530 were

mainly below 1500 MN/m^2 and were mainly red . In the case of “History of Tobias” c.16th century over half the threads tested were above 1500 MN/m^2,and included pink, black and blue threads. In “The Triumph of Time over Fame” c.1500-1530 most of the threads were below 1000 MN/m^2, and these included green, blue and beige. Characterisation of the dye used in the threads is being performed by other partners in the project.

4.1.2 Creep test

4.1.2.1 Immersion in water and heating

Figure 2 shows the percent displacement (black curve) measured against time (min). The upper figure shows the shrinkage behaviour of unaged parchment. Negative displacement corresponds to shrinkage of the parchment. The lower figure shows the behavior of a sample that has been subjected to accelerated ageing using NO_2 (50 ppm for 16 weeks) and combination of light (c.5.4 Mluxhrs) and heat (100 °C). The red trace gives the temperature profile and values can be read from the secondary Y axis (right). For the control sample shrinkage starts at about 55 °C and is complete at 80 °C when the sample is removed from water; for the aged sample shrinkage occurs almost immediately on immersion in water at 30 °C after initial expansion. The parameter measured is the amount of shrinkage that occurs. In the MAP project a ratio was calculated (main shrinkage / total shrinkage). The lower the value of this ratio the more damaged was the sample and the lower its shrinkage temperature. In the case of the aged sample in Figure 2 the value for the calculated ratio is c.0.4 (c.f to unaged c.0.8). This indicates that the damage caused by the ageing process was severe. Some of the historical samples from bookbindings and manuscripts have also been found to give low values for this ratio.

4.1.2.2. Controlled RH environment

The effect of increasing relative humidity (10-80% RH) on model woven (wool) tapestries (unaged red and black light aged 400 hrs/dosage 90Mluxhrs) is shown. Generally it was found that samples showed an initial expansion and that after 60% this was followed by a pronounced shrinkage. A ratio was calculated (shrinkage/expansion) and expressed in terms of a percentage relative to the undyed unaged control. The sample madder (RW2) is behaves significantly different from the

control sample as observed in Figure 1. Ageing produces a large change in the woven piece treated with oak gall mordant.

4.2 MICROTHERMAL ANALYSIS

A brief mention of some data will be made as this work is still in progress and will be reported in detail elsewhere. Figure 4 shows a selected area of aged parchment (32 days 80 °C and 40% RH) prepared as a thin section. Left hand side of Figure 4 shows the thermal conductivity image (50 µm x50 µm) at 50 °C. Dark areas correspond to areas of low thermal conductivity and brighter areas correspond to higher areas of thermal conductivity. In unaged parchment fewer darker areas have been observed and so at this stage there is an indication that darker areas are associated with more damage. The damage in parchment refers to gelatinised areas which have been observed by environmental scanning electron microscopy (Masic). The right hand side shows the corresponding thermomechanical curves for the numbered regions. Locations 3 and 5 (dark) have higher softening temperatures (which may correspond to more gelatinised areas) than locations 6 and 7. Thermal transitions of historical parchments have been recorded in the MAP project by DMTA and samples exhibiting transitions at higher temperatures have been associated with more gelatinised samples in comparison to transitions which occur at lower temperatures for samples where collagen is considered to be more intact (Odlyha 2002).

4.3 THERMOGRAVIMETRY

Thermal stability indices have been calculated from thermogravimetry for accelerated aged parchment samples and are shown in Figure 5. This was calculated from the weight loss which corresponds to the second major weight loss (between 400-530 °C) and this was normalised to correct for variations due to weight losses occurring at the lower temperatures. Similar procedure was used in the MAP project. Lowest values (and lowest thermal stability) were found for the light aged and light and heat (100°C) aged samples. RH and T ageing for 32 days at 60% RH 40C and 80% RH and 80°C4 also showed significant lowering of thermal stability. In the NO_2 aged series (exposure to 50ppm for periods between 2-16 weeks) the most affected was the sample aged for 16 weeks NO_2 with light and heat. It also showed a low shrinkage temperature and low shrinkage ratio (Figure 2).

4.4 DIFFERENTIAL SCANNING CALORIMETRY

To calculate the thermal stability index measurement is made of the ratio of the exothermic peak between 210-420 °C relative to the unaged silk thread sample. Lowering of this ratio occurs with light ageing (up to 16 Mluxhrs) and this is shown in Figure 6 which also shows values obtained from silk threads (sampled from the reverse side by conservators-restorers) from historical tapestries in collections in the Royal Palace, Madrid, Brussels and Bruges . Values indicate that the silk threads tested from tapestries PNM8 Atalanta y el jabeli de Calidonia Brussels 1620 and PNM5 Neoptolemo y Polxena,Brussels 1545 are in better condition than the others, in particular those from Brussels and Bruges.

5. CONCLUSIONS

In the case of tapestries it was found that the dyeing process already produces damage in the threads. Damage is readily measured and varying degrees of damage can be identified and used to assess the state of samples from historical tapestries. Damage assessment as developed in these measurements can lead to early warning of loss of strength in the threads, and can determine the length of time it remains on display. In the case of parchment samples additional data on characterisation of accelerated aged samples (including pollutant aged samples) have been obtained and this contributes to the damage atlas that is being established.

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Figure 1: Young's Modulus of unaged model woven tapestry (wool) samples. The coloured bars correspond to the dye colour: from left to right control, red dyes (madder ,madder, cochineal, Brazil wood where L is with lye), black, green (weld/woad), blue (woad) , mordants (alder bark tannin, alum, and oak gall), and yellow (YW2 dyer's greenweed, YW1 weld). Dyeing and mordanting processes affect the stiffness of the sample to varying degrees; most affected are GRW2(woad/weld dyed) YW1 (weld dyed) and mordant (oak gall). In the case of RW2 (madder) the presence of lye affects the sample stiffness (RW2L).

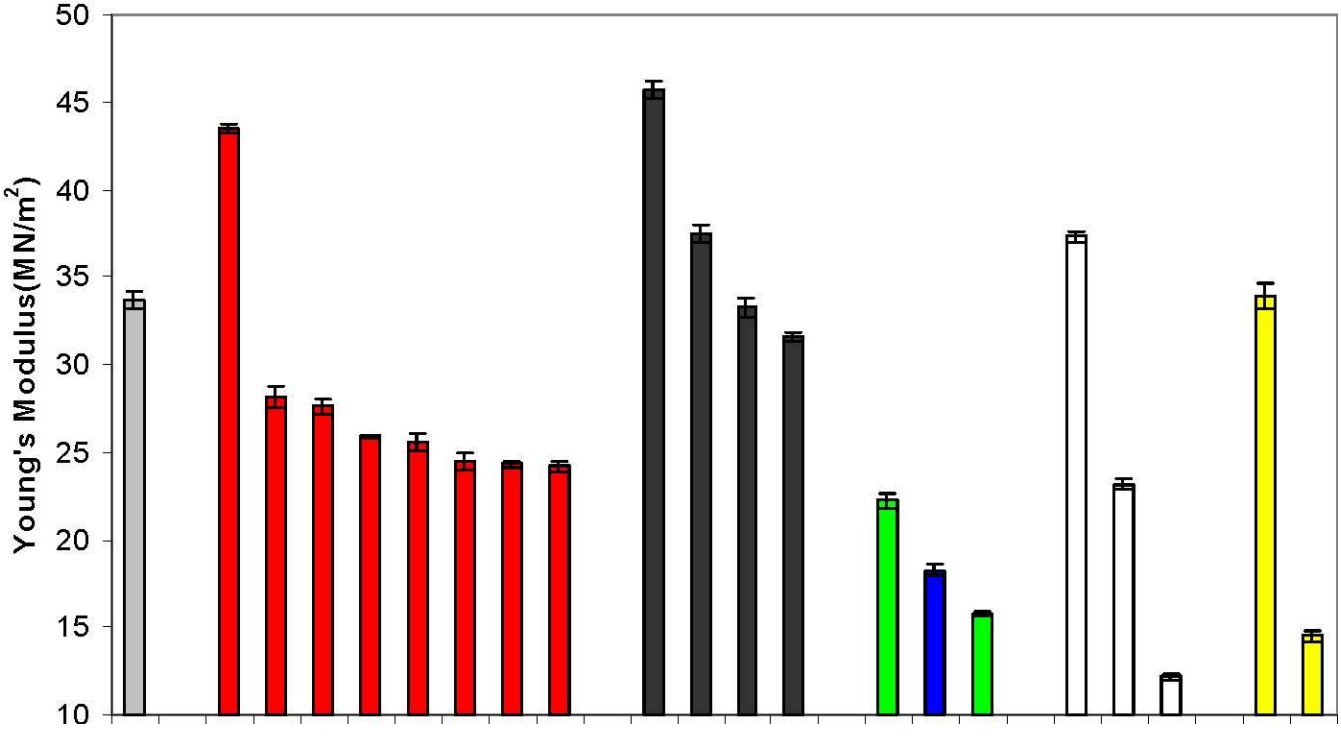
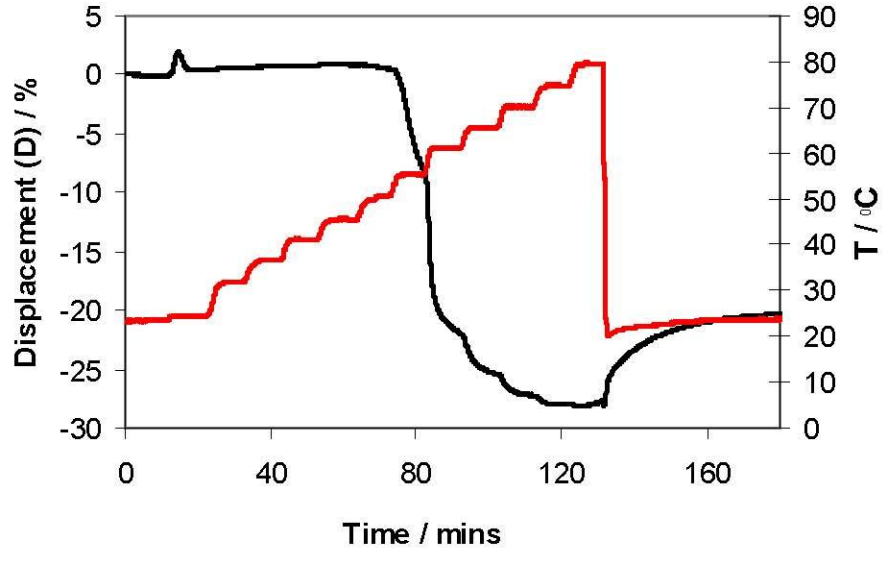


Figure 2: Displacement (%) (black curve) measured against time (mins). Upper figure is the unaged parchment sample and the lower figure is the light, heat and NO_2 aged sample. Negative displacement corresponds to shrinkage of the parchment. The red trace gives the temperature profile and values can be read from the secondary Y axis (right). For the control shrinkage starts at about 55 °C and is complete at 80 °C and the sample is removed from water; for the aged sample shrinkage occurs almost immediately on immersion in water at 30 °C.



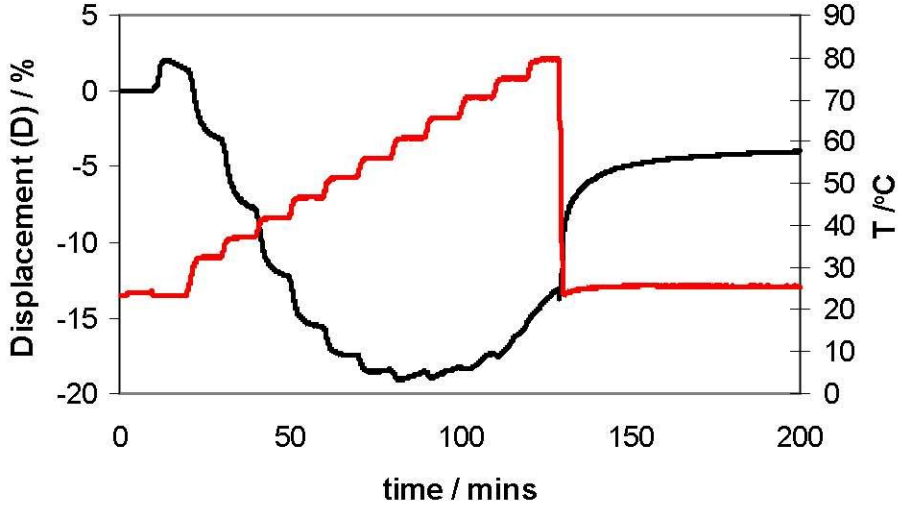


Figure 3: Effect of increasing relative humidity (10-80% RH) on model woven (wool) tapestries (unaged red and black light aged 400 hrs) expressed in terms of % (shrinkage/expansion) relative to the undyed unaged control.

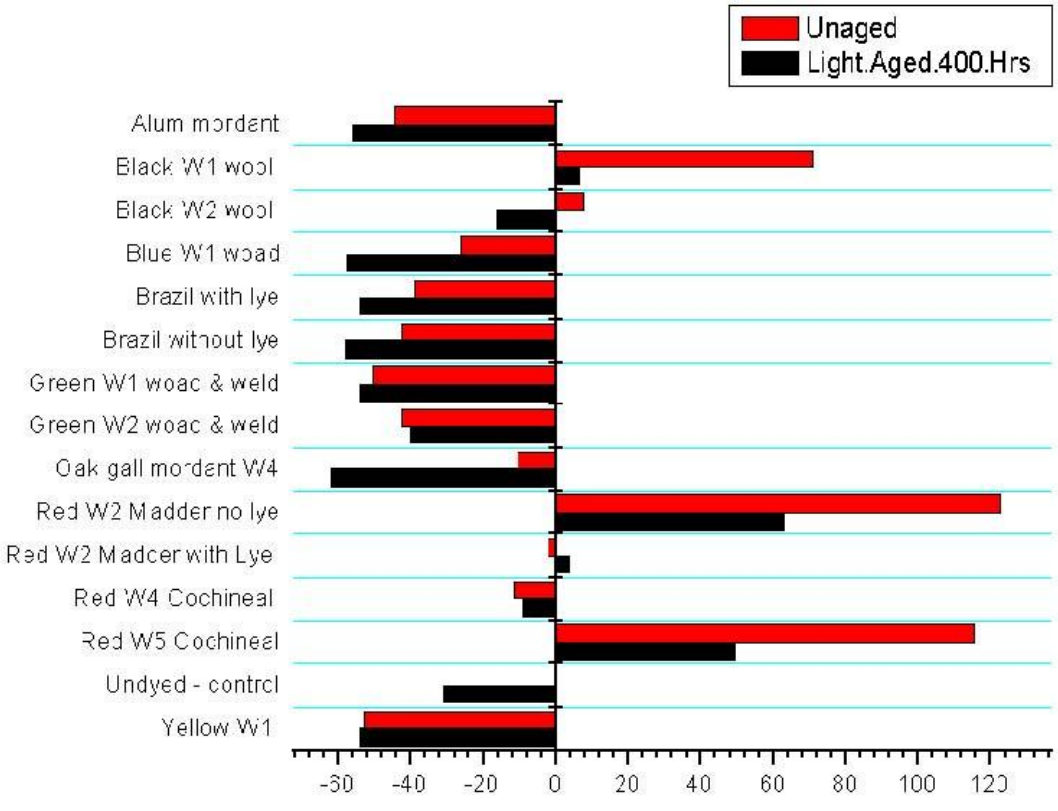


Figure 4: Microthermomechanical analysis of selected area of parchment sample (aged 32 days 80 °C and 40% RH). Left hand side is the thermal conductivity image (50 um x 50 um) at 50°C. Dark areas correspond to areas of low thermal conductivity and brighter areas correspond to higher areas of conductivity. In unaged parchment there are fewer darker areas and so an increase in darker areas may indicate more damage. The right hand side shows the corresponding thermomechanical curves for the numbered regions. Locations 3 and 5 (dark) have higher softening temperatures (which may correspond to more gelatinised areas) than locations 6 & 7.

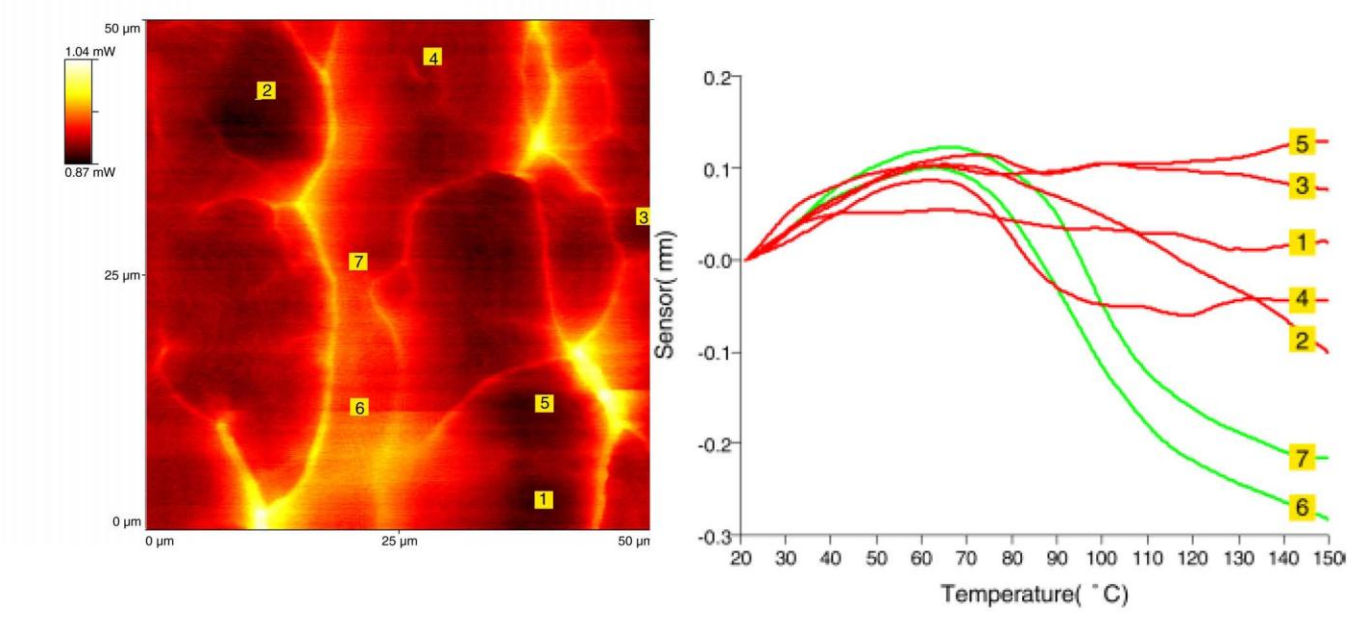


Figure 5: Thermal stability indices calculated from thermogravimetry for accelerated aged parchment samples. Lowest values are for light aged (5.4 Mluxhrs) and light & heat (100 °C) aged samples. RH and T ageing 32 days at 60% RH 40°C and 80% RH and 80 °C also show significant lowering of index. Of the NO_2 aged series (50 ppm) the most affected is the sample aged for 16 weeks NO_2 together with light and heat. It also shows a low shrinkage temperature (Figure 2).

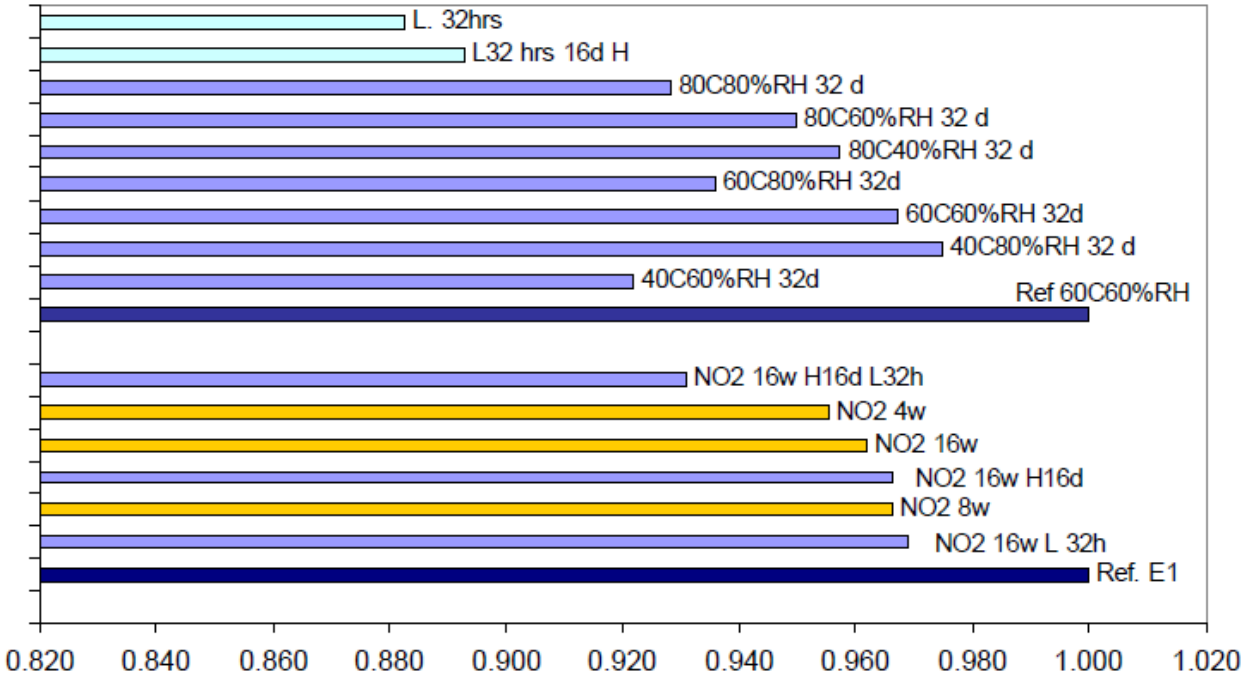


Figure 6: Thermal stability index calculated from differential scanning calorimetry for control and light aged silk samples (up to 16 Mluxhrs) and historical silk threads from tapestries Royal Palace Madrid [PNM1 Dedalo e Icaro, Brussels 1545,yellow bar corresponds to colour of sample), PNM2 Jupiter e Ganimede, Brussels 1545, (yellow and green bars correspond to colours of samples), PNM5 Neoptolemo y Polxena,Brussels 1545, PNM8 Atalanta y el jabeli de Calidonia Brussels 1620], BXL1 Justitia disarmed by Misericordia 1519-1524 Brussels (colour bar corresponds to sample colour), and BRU2 Mary's Dedication in the Temple 1639, Bruges (colour bar corresponds to sample colour).