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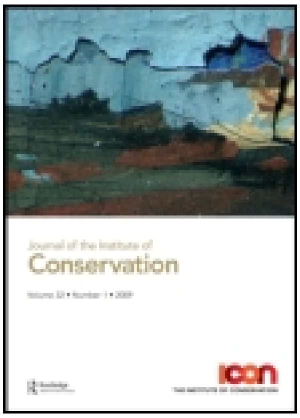

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Designing accelerated ageing experiments to study silk deterioration in historic houses

Naomi Luxford [a] & David Thickett [b]

[a] UCL Centre for Sustainable Heritage, Bartlett School of Graduate Studies, Central House 14 Upper Woburn Place, London, WC1H 0NN

[b] English Heritage, Ranger's House Chesterfield Walk, London, SE10 8QX E-mail: david.thickett@english-heritage.org.uk

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Designing accelerated ageing experiments to study silk deterioration in historic houses

Keywords
accelerated ageing; reciprocity principle; activation energy; deterioration rate; silk; experimental design

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This article presents the results of a study to develop an accelerated ageing methodology for the deterioration of historic silks. The research was part of a larger project investigating the deterioration of silk on open display in historic properties.[1] The aim of the larger research project was to determine the critical environmental factors causing silk deterioration, in order to improve preventive conservation methods for silk preservation. Natural ageing occurs over long time-scales with small incremental changes, which can be difficult to measure. Therefore, accelerated ageing aims to increase the deterioration rate over a shorter time-scale but cause changes large enough to be monitored. However, there is no universal method for accelerated ageing, making it difficult to compare studies on the same material, in this case silk.

This article discusses the development of an accelerated ageing methodology to study silk deterioration. The different types of ageing experiments and their use in studying silk deterioration are outlined. The selection of different environmental parameters is discussed and their extrapolation to real 'museum' environmental conditions demonstrated. The key observations about the experiments and equipment are presented, along with a note on the choice of analytical methods to determine the effectiveness of the ageing regimes.

This article does not discuss the results of the ageing experiments themselves, as these are discussed elsewhere.[2] However, by presenting the methodology, it is hoped that this will highlight the key points to consider when designing accelerated ageing experiments, both on silk and other materials found in historic collections. This will enable results from different studies to be compared more easily, widening the available literature on which decisions for the most suitable display environment for mixed media collections can be based.

1 Naomi Luxford, 'Reducing the Risk of Open Display: Optimising the Preventive Conservation of Historic Silks' (PhD diss., University of Southampton, 2009).

2 Luxford, 'Reducing the Risk'; Naomi Luxford, David Thickett, and Paul Wyeth, 'Applying Preventive Conservation Recommendations for Silk in Historic Houses' (paper presented at ICOM-CC Multidisciplinary Conservation: a Holistic View for Historic Interiors, Rome, March 23–6, 2010); Naomi Luxford, David Thickett, and Paul Wyeth, 'Preserving Silk: Reassessing Deterioration Factors for Historic Silk Artefacts', in *Proceedings of the Combined (NZ and AUS) Conference of the Textile Institute*, Dunedin, April 15–17, 2009 (New Zealand: The Textile Institute, 2009), 151–6.

The use of ageing experiments and comparison with natural ageing

To identify the critical factors causing deterioration over short time-scales accelerated ageing experiments are commonly used. This is because studying ageing processes under real conditions and time-scales is difficult. As Erhardt and Mecklenburg have noted, ageing experiments either have to occur over very long time intervals or very small changes must be measured and extrapolated.[3] By accelerating the ageing processes, quantifiable changes can occur over shorter time periods.

There are two general approaches: to mimic natural ageing as accurately as possible, or to increase reactions to understand a specific problem, for example as with the Oddy test. For the first approach, the reactions occurring during accelerated ageing should be the same as natural ageing. There should also be a similar increase in the reaction rate for all the deterioration reactions to ensure a different mechanism does not dominate.

3 David Erhardt and Marion F. Mecklenburg, 'Accelerated VS Natural Aging: Effect of Aging Conditions on the Aging Process of Cellulose', in *Materials Issues in Art and Archaeology IV*, ed. Pamela B. Vandiver et al. (Warrendale, PA.: Materials Research Society, 1995), 247–70.

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The aim of the experiments discussed in this article was to determine the critical environmental factors for silk deterioration occurring on open display; therefore, it was important to simulate natural ageing environments. However, a number of assumptions had to be made, which are common to these types of experiment. The first assumption was that the deterioration caused by accelerated ageing arises from the same reactions as those leading to natural ageing and these have been increased in rate similarly. Due to the complexity of natural polymers, such as silk, it is likely that multiple reactions are occurring under both natural and accelerated ageing. Therefore, the ageing experiments are used to give an holistic view and study how the series of reactions behave as a whole since this governs the change in physical properties.[4]

For the study presented here four environmental parameters were selected: visible light, visible light with ultraviolet (UV), temperature and relative humidity (RH). These were chosen primarily as they are those controlled most commonly within historic houses and, therefore, their effects on silk could be mitigated. These were studied using accelerated ageing experiments in a light chamber (visible light and visible light with UV) and in an oven (temperature and RH). However, for accelerated ageing there is no universal method, and two separate approaches have been used, in general, to relate the accelerated ageing experiments to display parameters.

For light ageing the reciprocity principle has been applied to calculate the length of ageing at much higher light levels than those used for display.[5] The reciprocity principle demonstrates that 10 hours at 50 lux is equivalent to 5 hours at 100 lux, both equalling 500 lux hours.

For the RH ageing presented here, the rate of deterioration is increased by using an elevated temperature. However, the use of elevated temperatures to increase the deterioration rate is common within accelerated ageing studies. Two further assumptions are then, in general, applied for the ageing experiments: that the deterioration processes occurring are chemical and that the increase in temperature will increase the rate of those chemical reactions. Using these assumptions, the Arrhenius equation can then be applied:

$$k = A\mathrm{e}^{-E_\mathrm{a}/RT}$$

where k is the rate constant, A the pre-exponential factor, E_a is the activation energy, R the gas constant and T the temperature (in K).

These assumptions have been discussed previously in relation to paper deterioration.[6] The determined activation energy is an average of the multiple reactions occurring; however, this is reported to remain linear.[7] Although there is no standard method, the approach presented in this study is similar to those used to study deterioration reactions for both paper and photographic media.[8]

The Arrhenius equation relates to reactions occurring in the gas or solution phase but has been applied to solid materials for various types of both paper and photographic media. The Arrhenius approach uses an elevated temperature to increase the rate of reaction, in this case silk deterioration. The activation energy of the reaction can be used to determine the increase in rate at the elevated temperature compared with room temperature. The deterioration caused by accelerated ageing can then be related to an equivalent display time, under the same RH. Appendix 1 contains a worked example of this calculation.

One of the aims of this study was to compare the different rates of deterioration created by the different ageing parameters. It is not uncom-

4 Douglas Nishimura, personal communication, March 28, 2008.

5 Garry Thomson, *The Museum Environment* (Oxford: Butterworth-Heinemann, 1986); David Saunders and Jo Kirby, 'Light-Induced Damage: Investigating the Reciprocity Principle', in *Preprints of the ICOM-CC 11th Triennial Meeting, Edinburgh, 1–6 September 1996*, ed. Janet Bridgland (London: James and James, 1996), 87–90.

6 H.Z. Ding and Z.D. Wang, 'Time–temperature Superposition Method for Predicting the Permanence of Paper by Extrapolating Accelerated Ageing Data to Ambient Conditions', *Cellulose* 14 (2007): 171–81; X. Zou, T. Uesaka, and N. Gurnagul, 'Prediction of Paper Permanence by Accelerated Aging I. Kinetic Analysis of the Aging Process', *Cellulose* 3 (1996): 243–67.

7 Erhardt and Mecklenburg, 'Accelerated VS Natural Aging'; Zou, Uesaka, and Gurnagul, 'Prediction of Paper Permanence'.

8 Erhardt and Mecklenburg, 'Accelerated VS Natural Aging'; Zou, Uesaka, and Gurnagul, 'Prediction of Paper Per-

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mon to see light ageing reported as the cause of greatest deterioration for a material but the light levels used to age over a short period quite often relate to a much greater display time than the thermal/RH ageing, thus making comparisons between light and RH ageing difficult. Using an equivalent display interval for the time axis rather than the actual accelerated ageing time enabled a direct comparison to be undertaken between the light and thermal/RH ageing regimes. For example, for the same accelerated ageing time, it was calculated that the increase in deterioration rates under visible plus UV light at 50 lux was 750 times the equivalent deterioration rates of room display conditions (20°C and 50 lux) and, at 50 lux without UV the equivalent, was 420 times room display conditions, whereas it was calculated using the Arrhenius equation that thermal ageing at 80°C would produce only 33 times more deterioration than at display room conditions. Therefore, light ageing (with or without UV) would lead to much greater deterioration when compared to thermal ageing over the same experimental time-scale, but this does not necessarily mean that it would lead to greater deterioration when extrapolated into equivalent display times. The use of equivalent display times enabled a better comparison of the different ageing regimes. This approach aimed to make the two very different methods of ageing (within a light chamber and an oven) comparable and relate the results more directly to the display of collections.

Experimental criteria

X-ray fluorescence (XRF) and scanning electron microscopy with energy dispersive spectrometry (SEM-EDS) were used to provide compositional analysis of silks from the English Heritage collection. This revealed that the majority of the collection is unweighted silk.[9] There is a small percentage (approximately 10%) of tin-weighted and high sulfur-content silk, with a few items that contain iron. To limit the number of variables, while maintaining results that are applicable to the collection, unweighted, undyed, plain-weave, medium-weight silk habutai was selected for the accelerated ageing experiments. Although light is known to cause fading of dyes,[10] its role in the deterioration of the silk substrate, which was the focus of this research project, is less well understood; therefore, undyed silk was used.

Five English Heritage properties had been selected for study based on their collections of silk on display. Analysis of four years' environmental monitoring data (2005–8) from the five properties (Audley End House, Apsley House, Brodsworth Hall, Osborne House and Ranger's House) highlighted which conditions were of interest for study. The RH levels tested in the experiments were selected from typical display environments, together with the two outer extremes of 0% and 100% RH. The display environments chosen were a low winter RH (30%), low average RH (40%), mid-average RH (50%), high average RH (60%) and high summer RH (75%). Light levels were chosen to reflect storage (0 lux), and the two maxima used to calculate annual light budgets for display (50 and 200 lux). A range of UV levels at 200 lux had originally been selected. However, it was not possible to create these ageing environments and, therefore, samples were light-aged at 200 lux with and without UV (at 350 μW lumen^{-1} in the light chamber used).

1 Temperature and RH experimental set up and calculations

1a Temperature

In designing the thermal and hydrolytic ageing experiments there are two factors to consider: what temperature to use and how to maintain the desired RH levels. The length of ageing required, and how long it relates

manence'; Alan M. Emsley and G.C. Stevens, 'Kinetics and Mechanisms of the Low-Temperature Degradation of Cellulose', *Cellulose* 1 (1994): 26–56; David D. Roberson, 'Permanence/Durability and Preservation Research at the Barrow Laboratory', in *Preservation of Paper and Textiles of Historic and Artistic Value II*, Advances in Chemistry Series 193, ed. John C. Williams and Joan M. Comstock (Washington, DC: American Chemical Society, 1981), 45–55; P.Z. Adelstein, 'Stability of Processed Polyester Base Photographic Films', *Journal of Applied Photographic Engineering* 7 (1981): 160–7; P.Z. Adelstein et al., 'Stability of Cellulose Ester Base Photographic Film: Part 1—Laboratory Testing Procedures', *Society of Motion Picture and Television Engineers (SMPTE) Journal* 101 (1992): 336–46; Adelstein et al., 'Stability: Part 2—Practical Storage Considerations', *SMPTE Journal* 101 (1992): 347–53; Adelstein et al., 'Stability: Part 3—Measurement of Film Degradation', *SMPTE Journal* 104 (1995): 281–91; Adelstein et al., 'Stability: Part 4—Behavior of Nitrate Base Film', *SMPTE Journal* 104 (1995): 359–69; Adelstein et al., 'Stability: Part 5—Recent Findings', *SMPTE Journal* 104 (1995): 439–47.

9 Luxford, 'Reducing the Risk'.

10 G.S. Egerton, 'Some Aspects of the Photochemical Degradation of Nylon, Silk, and Viscose Rayon', *Textile Research Journal* 18 (1948): 659–69; G.S. Egerton, 'The Action of Light on Viscose Rayon, Silk and Nylon, Undyed and Dyed with Some Vat Dyes', *Journal of the Textile Institute* 39 (1948): T293–T304; C.H. Giles and R.B. McKay, 'The Lightfastness of Dyes: a Review', *Textile Research Journal* 33 (1963): 527–77.

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to time on display, can be calculated based on the chosen elevated temperature. Selecting an appropriate temperature is important as the same reactions should occur during accelerated ageing as under real conditions. This is difficult to ensure but there are a number of factors that are likely to cause alterations to the type of reactions taking place. The first is the glass transition temperature, T_g. Above this point the properties of polymers change and, for most polymers, their reactivity will also change. For silk the T_g is around 160–175°C, depending on the species of silkworm.[11]

There is a further factor below the T_g that limits the upper temperature of ageing for silk. Silk contains both associated and bound water molecules within the crystalline region of its structure. The amount of associated water changes with RH and these are the effects being studied. However, the bound water can also be removed at high temperatures. This is likely to change the reactivity of silk as there will be a structural change upon the loss of the bound water. Therefore, ageing should occur below the point at which the bound water is lost. Silk is reported to undergo dehydration around 100°C; hence, the chosen temperature should be lower than this value.[12]

To prevent dehydration, but ensure a sufficient increase in the rate of reaction, 80°C was selected for the accelerated ageing tests. Prior to the accelerated ageing study presented here, a preliminary study was carried out.[13] This was required as the accelerated ageing experiments were to continue for twelve months and, therefore, could not be repeated easily. In the preliminary study, silk samples were aged at 50, 60, 70, 80 and 90°C and 30, 50 and 75% RH, for up to six weeks. Those samples aged at 90°C and 75% RH lost around 50% of their strength in six weeks. The results of the preliminary study were projected forward to indicate the deterioration that could be expected over the twelve months of the accelerated ageing. This showed that samples aged for more than six months would be too deteriorated to be tested after ageing. This preliminary study was useful to help to determine the experimental set up and the number of replicates required for analyses. The results of the preliminary experiments were also used to predict the remaining strength of samples after ageing at 80°C for a year (Fig. 1).

1b Relative humidity

There are a number of possible methods to create varying levels of RH for ageing environments. These include saturated salt solutions, humidity ageing chambers and glycerol solutions. Saturated salt solutions (and glycerol) control the RH by absorbing moisture from the air if the RH is higher than desired or releasing moisture if it is lower. The RH created depends on the salt chosen and the temperature at which the ageing experiments are carried out. There are two considerations with this technique: firstly, the solution has to be saturated at the ageing temperature in order to release or absorb moisture; secondly, the salts can migrate out of the solution.

Humidity ageing chambers can be set to create almost any RH level, within an operating temperature range. The accuracy of the maintained RH depends both on the equipment measuring the RH within the chamber (either a wet and dry bulb combination or an RH sensor, in which case regular calibration is required), and the mechanism by which the RH is controlled within the chamber. Some chambers can both humidify and dehumidify using mechanical plant to maintain the RH within a band (e.g. 50% ± 2% RH; therefore, when the RH is above 52% it will dehumidify). Others will humidify only and have limited (or no) capacity to dehumidify. This means a set point can be created but the chamber can not mimic fluctuating RH levels.

11 Jun Magoshi and Shigeo Nakamura, 'Studies on Physical Properties and Structure of Silk. Glass Transition and Crystallization of Silk Fibroin', *Journal of Applied Polymer Science* 19 (1975): 1013–15.

12 M.N. Bora, G.C. Baruah, and C.L. Talukdar, 'Investigation on the Thermodynamical Properties of Some Natural Silk Fibres with Various Physical Methods', *Thermochimica Acta* 218 (1993): 425–34.

13 Luxford, Thickett, and Wyeth, 'Preserving Silk'.

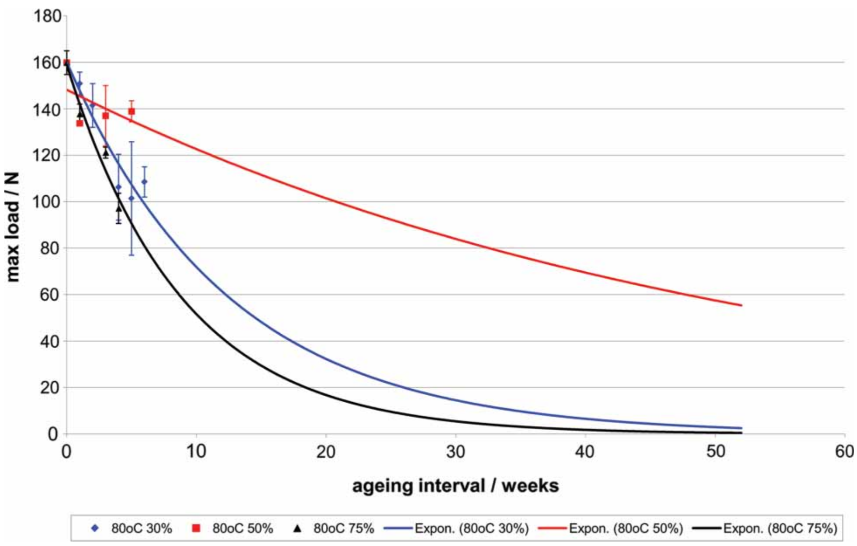

Fig. 1 Preliminary ageing results over six weeks projected forward to 52 weeks ageing (at 80°C) using Excel and exponential trend lines.

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Ageing with saturated salt or glycerol solutions is usually undertaken in sealed containers to ensure the RH is maintained. In humidity ageing chambers the samples are sealed within the chamber, with the size of the chamber itself limiting the number of replicates able to be aged at one time. The length of experiment provides a further limitation as only one RH level can be maintained at any one time. With the use of salt or glycerol solutions a number of RH levels can be set up and used simultaneously in different sealed containers within the same oven.

Humidity ageing chambers are relatively expensive, which limits their availability and so within conservation their use is often limited. However, one of their advantages is the limited extent to which gases evolved during deterioration are concentrated inside the chamber, depending upon its air exchange rate. In containers with soluble salt solutions, the evolved gaseous degradation products are sealed within the container, which can accelerate the deterioration reactions, sometimes dramatically.

Glycerol solutions can be prepared to create any RH level. Although it does not migrate in the way saturated salt solutions do, it is known to create a vapour phase.[14] This may contaminate the samples with glycerol. Therefore, with both saturated salt solution and glycerol methods there is the chance of contamination. However, glycerol is unlikely to be present under natural ageing conditions, whereas salt contamination is possible; hence, glycerol was rejected as a method of RH control in these experiments.

At 80°C most of the selected RH levels can be created with saturated salt solutions. However, in Greenspan's tables there is no quoted saturated salt solution to create 40% RH at this temperature.[15] Therefore, the 40% RH conditions were created using a humidity ageing chamber. The method of creating each RH level can be seen in Table 1.

1c Determining increase in rate of reaction

To determine the increase in the rate of reaction at 80°C the activation energy for the reaction was used. By rearranging the Arrhenius equation, the rate of reaction at room temperature can be compared with the rate of reaction at

14 http://www.dow.com/PublishedLiterature/dh_0032/0901b803800322bb.pdf?filepath=glycerine/pdfs/noreg/115-00677.pdf&fromPage=GetDoc (accessed August 3, 2009).

15 Lewis Greenspan, 'Humidity Fixed Points of Binary Saturated Aqueous Solutions', *Journal of Research of the National Bureau of Standards—A. Physics and Chemistry* 81A (1977): 89–96.

Table 1. Methods used to create RH levels and actual RH levels achieved.

RH level required (%)	Method/salt	Predicted RH (%)	Measured RH (± 1%)
0	Tubes oven dried, sealed at room temperature, then heated to 80°C	n/a	1.5
30	Magnesium chloride ($MgCl_2$)	26	29
40	RH oven	n/a	37
50	Sodium bromide (NaBr)	51	53
60	Potassium iodide (KI)	61	62.5
75	Sodium chloride (NaCl)	76	79
100	Liquid water	n/a	96

Note: All are at 80°C.
The RH levels for the saturated salt solutions were predicted from the literature.[16]

80°C.[17] The increase in rate (k) can then be used to determine the length of ageing required. For example, if ageing at 80°C causes a ten-fold increase in the rate of reaction, then one year of accelerated ageing is equivalent to 10 years on display.

One problem with this method is the reliance on the activation energy to determine the length of ageing. The preliminary study indicated that the activation energy for silk deterioration was approximately 50kJ mol^{-1}.[18] Using the Arrhenius equation, this leads to an increase in deterioration rate at 80°C of almost 33 times that of room temperature (Appendix 1). Therefore, a sample aged for one month at 80°C would be equivalent to almost three years on open display at 20°C.

When using the same approach for substances other than silk the rate would have to be recalculated based on the activation energy for their deterioration. This value is not always available in the literature or, as is the case for silk, a wide range of values can be reported (10–150kJ mol^{-1}).[19]

1d Experimental set up

The silk samples (25mm × 100mm, warp in the longest direction) were placed in hybridization tubes with the relevant saturated salt solution, as illustrated in Fig. 2. Six samples of silk were placed in each tube, to ensure the repeatability of sample analysis after ageing. For samples aged at 0% RH, glass wool was included for consistency, although nothing was placed beneath it. The hybridization tubes were 150mm long and the silk samples were suspended approximately 2mm from the top. The salt solutions normally occupied the bottom 20mm, with the glass wool (depth approximately 10mm) directly above this. For 100% RH, liquid water replaced the saturated salt solution, as recorded in Table 1. The hybridization tubes were then placed in either a Binder APT heating and drying oven or Heraeus Kendro UT6P air circulation oven. Both were set to 80°C and were reported to fluctuate by ±3°C.

The 40% RH samples were suspended from a shelf within the Espec SH-221 bench top temperature and humidity chamber. This was set to 80°C (± 0.3°C) and 40% RH (±3% RH). All samples were aged in the dark and were given an identification code with the letter D. This code started with the ageing RH (0, 30, 40, 50, 60, 75, 100), the letter D and then the length of ageing in months (1, 2, 3, 6, 9, 12). For example, a sample aged for three months at 40% RH was given a code of 40D3.

1e Testing RH levels produced

The saturated salt solutions within the hybridization tubes required occasional additional water or salt, suggesting that they were not perfectly sealed. Therefore, the stability of the saturated salt solutions within the hybridization tubes was tested and the actual RH level for each of the chosen RH conditions determined. To monitor the environment within

16 Greenspan, 'Humidity Fixed Points'.

17 20°C was selected to represent room temperature, as this is the annual average room temperature in the English Heritage properties studied.

18 Luxford, Thickett, and Wyeth, 'Preserving Silk'.

19 Bora, Baruah, and Talukdar, 'Investigation on the Thermodynamical'; Paul Garside and Paul Wyeth, 'Characterization of Silk Deterioration', in *Strengthening the Bond: Science and Textiles Preprints* ed. V.J. Whelan, North American Textile Conservation Conference, April 5–6, 2002, 55–60; Keith R. Millington, George Maurdev, and Michael J. Jones, 'Thermal Chemiluminescence of Fibrous Proteins', *Polymer Degradation and Stability* 92 (2007): 1504–12; Vincent Daniels and Morven Leese, 'The Degradation of Silk by Verdigris', *Restaurator* 16 (1995): 45–63; Eric F. Hansen and William S. Ginell, 'The Conservation of Silk with Parylene-C', in *Historic Textile and Paper Materials II—Conservation and Characterization* ed. S. Haig Zeronian and Howard L. Needles, American Chemical Series 410 (Washington, DC: American Chemical Society, 1989), 108–33.

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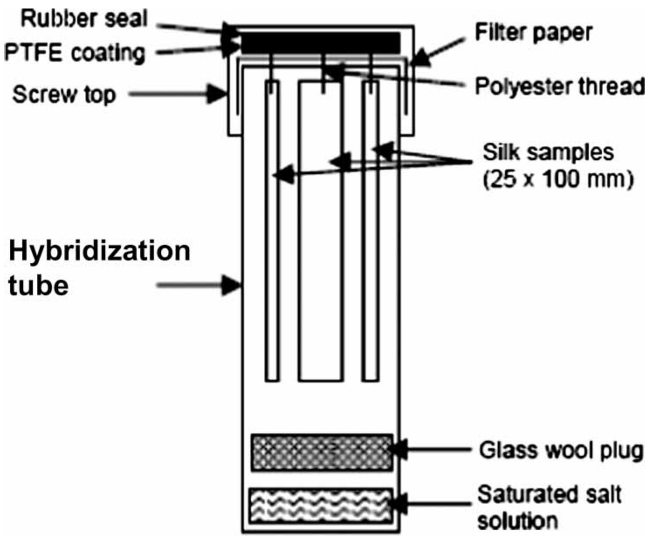

Fig. 2 Diagram of the thermal and RH ageing experimental tubes containing the silk samples and relevant saturated salt solution.

the sealed tube a hole was drilled through the lid and the polytetrafluoroethylene- (PTFE-) coated rubber seal of a hybridization tube. A Rotronic HygroClip SC05 temperature and humidity probe was inserted through the lid and seal and the top of the probe sealed to the outside of the hybridization tube lid using a silicone sealant (Fig. 3). This was connected to a Rotronic HygroPalm 2 and a laptop running the HW3 software to record temperature and RH every five minutes for a week.

A hybridization tube was prepared as for the main RH and temperature experiments with an appropriate saturated salt solution, but with the probe attached through the lid, and then placed in the ageing oven at 80°C for one week. This was repeated for each different saturated salt solution and RH level. The probe was also placed in the humidity ageing chamber for one week. The results of this test can be seen in Table 1; depending on the salt used the monitored values varied by 1% to 3% from those predicted by the literature.[20] The sensor within the hybridization tube recorded a

20 Greenspan, 'Humidity Fixed Points'.

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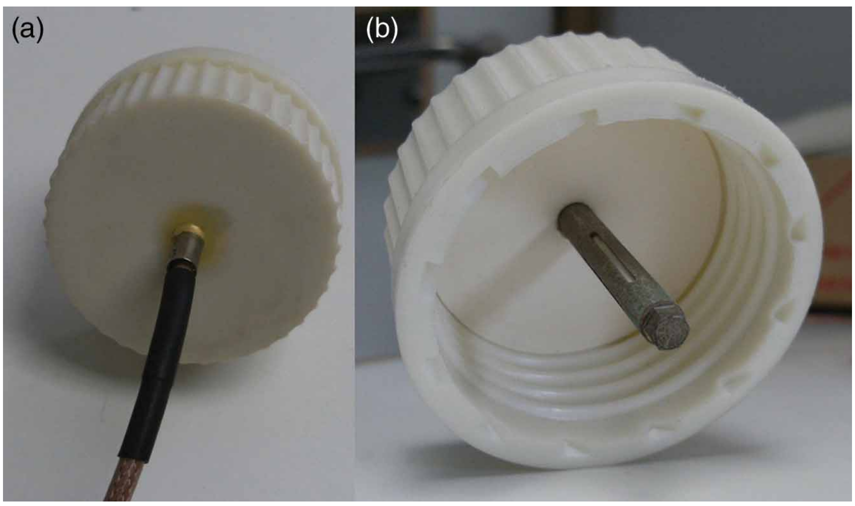

Fig. 3 RH probe inserted through hybridization tube lid for saturated salt test: (a) silicone seal around the outside of the lid; (b) the probe inside the lid.

1% RH variation during the week-long tests, implying that conditions were stable over shorter time periods. However, the results were applicable only as long as the water levels were maintained, as the hybridization tubes still required additional deionized water to maintain the saturated salt solutions. Generally, the values measured were close to those reported and offered an acceptable range of RH values for the study.

2 Light experimental set up and calculations

The length of time required for light ageing can be calculated relatively simply due to the reciprocity principle. For English Heritage properties annual light budgets are set for each display area. These take into account the opening hours and collections in each room. The annual light budgets are calculated based on two different maxima, 50 lux for light-sensitive materials (146,100 lux hours per year) and 200 lux for general collections (584,400 lux hours per year). Within the houses light levels are controlled using double blinds at the windows. The blackout blind and lighter-coloured blind can be positioned to alter the light level, reduce the incoming light and prevent direct sunlight on objects.

Light ageing was carried out in a custom-made light box from Complete Lighting Systems (Fig. 4). The light box contained 12 F20W/AD artificial daylight fluorescent lamps. These lamps are specifically designed to replicate daylight effects, with a high colour temperature (6500K) and good colour rendering index ($Ra = 92$).[21] This is desirable as English Heritage properties are lit using natural light supplemented by artificial lighting when required.

21 www.gelighting.com (accessed May 26, 2011).

Light levels in the light ageing chamber were measured at 7000 lux beneath the UV filter, and a UV level of 2 μW lumen^{-1}. For each chosen display time interval, the number of years was multiplied by the annual light budget in lux hours to calculate a total required exposure, for both 50 and 200 lux maxima. The total exposure was then divided by the ageing light level (7000 lux) to give a number of ageing hours. For example, four years on display at 200 lux gives 2,337,600 lux hours exposure. To obtain this in the light chamber, ageing at 7000 lux required 334 hours or approximately 14 days. The reciprocity principle was used to reduce the number of samples used in the light experiments, due to limited space in the light box. As 2 years at 200 lux is the equivalent of 8 years at 50 lux, some samples were used to provide data for different time intervals at both 50 and 200 lux.

Ultraviolet-absorbing film is fitted to all windows within the selected English Heritage properties, reducing the UV light levels inside the rooms. It was originally hoped to examine a range of UV levels to determine the effects of different UV levels on silk ageing. However, the light box design meant that it was not possible to vary the UV levels without obtaining different UV filters. Therefore, it was decided to expose samples above and below the UV filter already in the light box, thus exposure would be at only one UV level. As the UV filter also reduced the amount of transmitted light on the samples under the UV filter, the calculations were adjusted to ensure the same equivalent display time-scale was used both with and without UV. The light level above the UV filter was measured as 12,500 lux and 350 μW lumen^{-1}.

As light ageing is unlikely to occur in isolation on open display, it was decided to carry out these experiments at a range of RH levels. This would also highlight any possible synergistic effects between light and RH. However, to reduce the length of experiments and number of samples to be analysed, low (30%), middle (50%) and high (75%) RH values, based on display conditions, were selected for light ageing. To maintain the RH levels during the light-ageing experiments, saturated

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Fig. 4 The light ageing chamber. The UV filter and plastic bowl containing a saturated salt solution can be seen inside the chamber.

salt solutions were placed in an open plastic container inside the light box. This was half filled and a perforated covering placed over it to reduce possible salt migration. The UV ageing was carried out solely at the middle RH to reduce the number of samples, while still providing a comparison with the other ageing conditions. RH levels were checked weekly and the salt solutions maintained as and when required to keep the RH at the desired level. The light box operates at ambient room temperature (22 ± 2°C), using fans in the lid to reduce heating from the bulbs.

The samples were again given identifying codes based on the ageing conditions. These began with the RH level (30, 50 or 75) and then L or UV to indicate light ageing with or without UV radiation, respectively. This was followed by the maximum light level used to calculate the annual light budget (50l or 200l), where l indicates lux. The final number indicates the equivalent number of years on display created during ageing (2, 4, 6, 8, 15 or 16). For example 30L50l6 indicates samples were light aged at 30% RH for the equivalent of six years on display at a maximum light level of 50 lux.

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RH ageing problems

Despite the glass wool in the hybridization tubes, which was intended to act as a barrier above the saturated salt solution, salt migration was still observed. In some cases the silk samples had heavy deposits of salt on them, making the silk brittle and, if they stuck to the sides of the hybridization tube, likely to break. From the preliminary experiments, salt contamination had affected results, in particular the tensile testing analysis, altering the shape and breaking point of the sample and leading to samples being excluded from the results.

To overcome this problem the salt deposits were rinsed out of silk samples with deionized water after ageing. However, as not all samples were rinsed (only those visibly covered with salts), this potentially introduced a further variable that needed to be taken into consideration in the final results.

One of the saturated salts produced an unexpected change. To create an environment of 60% RH a saturated solution of potassium iodide had been used. However, after six months of ageing, the silk samples were dark brown in colour. Inside the hybridization tubes, although a saturated salt solution remained, it was no longer a white salt with clear liquid but a yellow solid in a brown solution. The smell when removing the lids, and appearance, was similar to iodine solution, which had seemingly 'dyed' the samples suspended above. The later ageing samples were observed more closely and samples with half the length appearing 'dyed' were noted (Fig. 5). The longer the samples were aged, the further up the length of the sample the 'dyeing' progressed. This contamination had an effect on the tensile strength of these samples leading to deterioration similar to samples aged at an RH higher than 60%.

Although the humidity ageing chamber removed the possibility of salt contamination, some of the samples aged in the humidity chamber had small areas missing after ageing (Fig. 6). These seemed to be burn marks from contact with the metal wire shelf as the samples were blown upwards towards the wire shelf by the circulation fan. This had not been anticipated, as the lower shelf had been removed and samples suspended from the filter paper to hang freely beneath the upper shelf. An effect of this damage was reduced tensile strength of these samples, as missing areas introduced weaknesses into the affected samples. In some cases the damage was so great that the number of available replicates for analysis after ageing was reduced as the missing areas shortened the length of some samples to less than the gauge length of the tensile tester.

Yellowing during accelerated ageing is commonly observed for a range of materials.[22] During the preliminary tests greater yellowing had been observed with increasing temperature. During the longer-term ageing (up to one year at 80°C), different levels of yellowing were also observed. The amount of yellowing increased with increasing RH. However, samples aged in the humidity chamber for 12 months seemed to have yellowed less than those aged at 30% RH using a saturated salt solution.

22 H.R. Richards, 'Thermal Degradation of Fabrics and Yarns Part 1: Fabrics', *Journal of the Textile Institute* 1 (1984): 28–36; Capucine Korenberg, 'The Effect of Ultraviolet-filtered Light on the Mechanical Strength of Fabrics', *The British Museum Technical Research Bulletin* 1 (2007): 23–7; Hansen and Ginell, 'The Conservation of Silk'.

Selection of analytical techniques

When designing accelerated ageing experiments it is crucial to determine what information you require and what techniques might be able to give you these data, before ageing takes place. This means the sample size and number of replicates can be adjusted accordingly and, where necessary, alternative analytical techniques sought. It is also important to determine whether you can undertake this analysis yourself or require someone else to analyse the samples, as well as determining the availability of the equipment. Preliminary experiments can be useful in understanding these questions and, more importantly, their solutions. For this research a literature search helped to identify techniques that had been used previously to

Fig. 5 Samples 'dyed' after accelerated ageing at 60% RH for two months using potassium iodide.

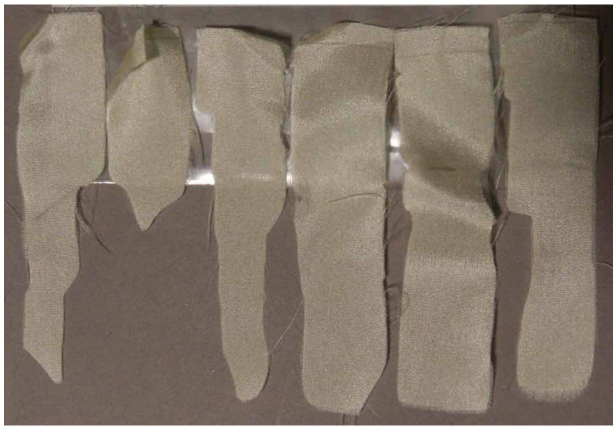

Fig. 6 Missing areas of samples after nine months' ageing in the humidity chamber.

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analyse silk, including the sample size needed for analysis and the type of information produced. The analytical techniques selected affected the sample size and numbers of replicates used during the accelerated ageing experiments.

Conclusion

Some of the issues with using accelerated ageing experiments include questions regarding whether the same reactions are occurring under natural and accelerated ageing conditions, and whether the increased deterioration rates under accelerated ageing conditions can be extrapolated to natural ageing conditions. Further questions relate to the magnitude of the change occurring during ageing and whether this can be measured, how the ageing environments are related to display conditions, what ageing conditions should be used and how to replicate the variables found on display without creating such a large number of experimental variables that analysis is too complex to interpret meaningfully.

In contrast, there are a number of benefits to accelerated ageing experiments, including that they provide data without damaging objects. These types of experiment can also demonstrate the key display parameters to target improvements in preventive conservation as well as highlighting further research needed for collections. Accelerated ageing can be made more relevant and easier to relate to the collections by taking objects and their display parameters as the basis for ageing experiments. Finally, comparison between analytical results from historic materials and accelerated aged samples can confirm whether the artificial deterioration created is similar enough to validate the results of the ageing study.

This article outlines a methodology used for accelerated ageing experiments to study silk deterioration. It is by no means the only ageing technique available in deterioration studies. However, it provides a way to compare different ageing mechanisms and compare them with deterioration mechanisms acting on objects on open display. In this case the methodology was used to produce preventive conservation recommendations for historic silk on open display.[23]

This approach could be adapted easily for use with other materials common to historic collections. As long as the reactions occurring are chemical then the Arrhenius equation can be applied, as here, by changing the activation energy to that of the material being studied. Generally the equipment is not high-tech and could be replicated or modified (such as using boiling tubes and glass

23 Luxford, Thickett, and Wyeth, 'Applying Preventive Conservation Recommendations'.

stoppers instead of hybridization tubes) by most people with access to an oven for ageing. By considering the points discussed in developing this accelerated ageing methodology it is hoped that the results of other ageing studies can be made easier for comparison. This would increase the available data upon which preventive conservation decisions for the optimum environmental conditions for mixed media displays are based.

Appendix 1

The Arrhenius equation can be rearranged to determine the increase in rate of reactions.

$$k = A\mathrm{e}^{-E_a/RT} \tag{1}$$

where k is the rate constant, A the pre-exponential factor, E_a is the activation energy, R the gas constant (8.314J $\mathrm{mol}^{-1}\,\mathrm{K}^{-1}$) and T the temperature (in K = temperature in °C + 273).

$$k/A = \mathrm{e}^{-E_a/RT} \tag{2}$$

Using Equation 2 and the values for these experiments [E_a = 50kJ mol^{-1} (50,000J mol^{-1}), room temperature is 20°C (293K) and the ageing temperature 80°C (353K)], we can determine k/A at 20°C and 80°C and then the increase between the two.

At 20°C $k/A = e^{[-50000/(8.314*293)]} = e^{-20.5} = 1.22 \times 10^{-9}$
At 80°C $k/A = e^{[-50000/(8.314*353)]} = e^{-17} = 3.99 \times 10^{-8}$

The increase in rate between the two is $3.99 \times 10^{-8}/1.22 \times 10^{-9} = 32.7$ or approximately 33 times, hence one years' accelerated ageing is approximately equal to 33 years on open display.

The pre-exponential factor, A, can be ignored in this example, as over such a small temperature difference, it is approximately constant. Whether there is a temperature dependence of A is still under debate in the literature.

This equation can be used for other materials and ageing experiments by simply changing the activation energy value (E_a in J) and the ageing and room temperature values (in K).

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Jim Reilly and Doug Nishimura of the Image Permanence Institute have provided information, assistance and discussion on various aspects of this research which was greatly appreciated. I would also like to acknowledge the Arts and Humanities Research Council (AHRC) for funding the research.

Abstract

An accelerated ageing methodology to study silk deterioration is presented. This draws on approaches used in paper and photographic conservation, although the references are not widely available within conservation. The experiments were designed based on the English Heritage silk collection and its display environment. The selection of different light and humidity conditions for ageing will be discussed, including the experimental parameters and equipment. Details on how the ageing time was related to an equivalent display time will be demonstrated. Some of the key observations and problems which occurred during the project will also be outlined. Some of the advantages and disadvantages of using accelerated ageing experiments to study deterioration reactions will be reported.

Résumé

«Concevoir des expériences de vieillissement accéléré pour étudier la détérioration de la soie dans des maisons historiques»

Une méthodologie de vieillissement accéléré destinée à étudier la détérioration de la soie est présentée. Elle s'appuie sur les approches employées dans la conservation du papier et des photographies même si les références ne sont pas largement disponibles dans ce domaine. Les expériences ont été conçues autour de la collection de soies du English Heritage et de ses conditions d'exposition. Le choix de différentes conditions d'éclairage et d'humidité pour le vieillissement ainsi que les paramètres expérimentaux et l'équipement seront expliqués. La façon dont le temps de vieillissement a été relié à un temps d'exposition équivalent sera démontrée. Quelques-unes des principales observations et les problèmes survenus au cours du projet seront également exposés. Le choix des méthodes d'analyse sera présenté, ainsi que la comparaison des résultats pour déterminer l'efficacité du traitement de vieillissement utilisé. Quelques avantages et quelques inconvénients de l'utilisation d'expériences de vieillissement accéléré pour étudier les réactions de détérioration seront signalés.

Zusammenfassung

„Entwicklung beschleunigter Alterungsverfahren zur Untersuchung des Degradationsverhaltens von Seide in historischen Häusern"

Vorgestellt werden beschleunigte Alterungsverfahren zur Untersuchung der Degradationserscheinungen von Seide. Das Verfahren beruht auf Ansätzen aus der Papier- und Fotografierestaurierung, wobei die Quellen in der Restaurierungsliteratur allgemeinhin nicht sehr bekannt sind. Die Versuche wurden für die Seidensammlung des English Heritage und dessen Ausstellungsbedingungen konzipiert. Verschiedene Licht- und Feuchtigkeitsbedingungen für die beschleunigte Alterung, sowie Versuchsaufbau und Versuchsparameter werden diskutiert. Details zur Korrelation zwischen Alterungszeit und entsprechender Ausstellungsdauer, sowie Schlüsselbeobachtungen und Probleme wðhrend der Versuche werden ebenfalls erörtert. Die Auswahl analytischer Verfahren wird vorgestellt und ein Vergleich der Versuchsergebnisse zur Begutachtung der Effektivität des jeweils gewählten Alterungsverfahrens besprochen. Abschlieβend werden Vor- und Nachteile der Anwendung beschleunigter Alterungsverfahren zur Untersuchung des Degradationsverhaltens von Seide diskutiert.

Resumen

"Diseñando experimentos de envejecimiento acelerado para estudiar la deterioración en casas históricas"

Se presenta una metodología de envejecimiento acelerado para estudiar la deterioración de la seda recurriendo a enfoques usados en la conservación de papel y fotografías, aunque las referencias no son fáciles de conseguir dentro de la conservación. El diseño de estos experimentos esta basado en la colección y el medio ambiente de las exposiciones de la colección de seda perteneciente al English Heritage. Se hablará de la selección de distintas condiciones de luz y de humedad para el envejecimiento, incluyendo parámetros experimentales y equipo. También se demostraran detalles de cómo el tiempo de envejecimiento ha sido relacionado con el tiempo equivalente de exposición. Se resumen algunas de las observaciones y problemas que ocurrieron durante el proyecto. Se presentará la elección de métodos analíticos junto con la comparación de los resultados para determinar la efectividad del sistema usado. Se reseñarán algunas de las ventajas y desventajas en el uso de experimentos de envejecimiento acelerado para estudiar las reacciones de deterioración.

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Biographies

Naomi Luxford is a post-doctoral research fellow at the Centre for Sustainable Heritage, University College London. This research was completed as part of Naomi's PhD studies at the Textile Conservation Centre in collaboration with English Heritage. Her thesis entitled 'Reducing the Risk of Open Display: Optimising the Preventive Conservation for Historic Silks' was completed in 2009. She graduated from the RCA / V&A Conservation MA programme in 2006 and has an MSci in Chemistry from the University of Bristol. Naomi is currently researching damage to decorative furniture surfaces in historic houses with changing climate, funded by the AHRC / EPSRC Science and Heritage Programme.

David Thickett is Senior Conservation Scientist at English Heritage. David graduated in Natural Sciences from Cambridge University in 1988. He worked in industrial research, high performance ceramics for two years before joining the conservation science group of The British Museum, where he specialized in metals, ceramics, glass and stone deterioration and conservation, including significant analytical experience. He was also responsible for general preventive conservation research and implementation. He became Senior Conservation Scientist with English Heritage in 2003. He is responsible for the preventive conservation research programme and environmental preventive conservation standards across 130 sites and 500,000 collection objects of all types. His current research interests include painting microclimate frames, showcases, RH susceptibility of rigid organic objects, sustainability and environmental standards. He is a directory board member for the Infra-red and Raman User Group, assistant coordinator of ICOM-CC Preventive Conservation Working Group (coordinator 2002–5), UK management committee member and working group chair of COST action D42 Enviart (the effects of indoor environment on heritage collections), and a UK expert to CEN TC 346 working group 4 (environment).

Materials and suppliers

Habutai Silk Medium:
Whaleys (Bradford) Ltd
Harris Court
Great Horton
Bradford
West Yorkshire BD7 4EQ
UK

Light chamber with 12 GE F20W/AD artificial daylight fluorescent bulbs, polycarbonate UV filter and 4 SUNON SF23092A fans:
Complete Lighting Systems
7 Park Industrial Estate
Frogmore
St. Albans
Hertfordshire AL2 2DR
UK

RH salts and Wheaton Hybridization Bottles (Tubes) 35mm × 150mm:
Fisher Scientific UK Ltd
Bishop Meadow Road
Loughborough
Leicestershire LE11 5RG
UK

Heraeus Kendro UT6P Air Circulation Oven:
Kendro Laboratory Products Ltd
Bishop's Stortford
Hertfordshire
UK

RH oven (ESPEC SH-221):
ESPEC North America, Inc.
4141 Central Parkway
Hudsonville
MI 49426
USA

Contact addresses

Naomi Luxford
UCL Centre for Sustainable Heritage
Bartlett School of Graduate Studies
Central House
14 Upper Woburn Place
London WC1H 0NN
Email: n.luxford@ucl.ac.uk

David Thickett
English Heritage
Ranger's House
Chesterfield Walk
London SE10 8QX
Email: david.thickett@english-heritage.org.uk

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