Preventing silver tarnish – lifetime determination of cellulose nitrate lacquer

Naomi Luxford and David Thickett*

English Heritage, 1 Waterhouse Square, 138 Holborn, London, EC1N 2ST, United Kingdom

* Corresponding author: naomi.luxford@english-heritage.org.uk

Abstract

Silver artefacts on open display are often protected from tarnishing using cellulose nitrate lacquers. Cleaning and relacquering is time consuming and has damaging long term effects over many repetitions. Hence optimisation of the period between treatments is of great interest.
The lacquer degrades over time, diminishing the protective effect and the effective lifetime is unknown. Aesthetic effects and the loss of reversibility can also affect the lifetime of the coating. Cellulose nitrate lacquered sterling silver coupons were used to replicate silver collections in museums, specifically the Portuguese Centrepiece at Apsley House. The effects of light and varying relative humidity (RH) levels on deterioration were studied using accelerated ageing. Fourier transform infrared (FTIR) analysis indicates cellulose nitrate lacquer is effective in protecting silver against tarnish after 20 years equivalent light ageing and at least 10 years equivalent ageing in low and mid RH environments. The lacquers remained soluble in acetone after the ageing regime.

Keywords: silver, tarnish, cellulose nitrate, lacquer, Frigilene, preventive conservation

Introduction

The Portuguese Centrepiece at Apsley House forms the centre of the Portuguese Service, which includes hundreds of items of silver and silver-gilt table ware. The Portuguese Service was presented to the 1st Duke of Wellington in 1816 to celebrate the victory of the triple alliance against Napoleon's forces in the Peninsular War. Designed by Portuguese court painter Domingos Antonio de Sequira the Centrepiece is massive in scale, around eight metres long, a metre wide and half a metre tall, it features many highly ornate and intricate pieces (see figure 1). Originally it could only be seen once or twice a year by chosen guests but since being presented to the nation in 1947 it has been on continuous open display. To prevent silver tarnish forming the Centrepiece has been lacquered with cellulose nitrate. This was most recently undertaken in 1995 and it was thought this would need replacing soon. To determine whether relacquering was required it was desirable to determine the effective lifetime of cellulose nitrate lacquer in preventing silver tarnish.

Figure 1: Portuguese Centrepiece, Apsley House (English Heritage)

Whilst there has been a significant amount of research on the deterioration of cellulose nitrate, very little has been published on the effective lifetime of it as a lacquer on silver. Most research on cellulose nitrate deterioration has focussed on its use as an adhesive (Shashoua et al. 1992) or as a plastic (Derrick et al. 1994; Stewart et al. 1996). De Witte (1973) compared a number of varnishes including cellulose nitrate and found it yellowed and was damaged by ageing. However the accelerated ageing conditions used are very harsh and not representative of indoor conditions so may not reflect deterioration within museum environments. Reedy et al. (1999) compared Agateen, a cellulose nitrate lacquer, with two acrylic coatings for silver and found Agateen performed best. However this work did not offer an effective lifetime of the coatings tested.

Experimental

To study this further, accelerated ageing experiments with cel-

Table 1: Accelerated ageing conditions and the identifying codes used for samples

equivalent ageing years	light ageing	hydrolytic ageing experiments		
		low RH	mid RH	high RH
2	light 2	low 2	mid 2	high 2
5	light 5	low 5	mid 5	high 5
10	light 10	low 10	mid 10	high 10
15	light 15	low 15	mid 15	high 15
20	light 20	low 20	mid 20	high 20

lulose nitrate lacquered, sterling silver coupons were used to replicate silver collections in museums, specifically the Portuguese Centrepiece at Apsley House. Feller (1994) discussed in some detail the problems associated with accelerated ageing, but the conditions used for this work were selected to best represent those experienced by this object. Sterling silver (92.5% silver, 7.5% copper) was chosen as it is close to the composition of the Centrepiece (91% silver, 9% copper) as analysed with X-ray fluorescence (XRF) by MOLAB. The coupons were degreased with acetone and a single coat of Frigilene lacquer brushed on one side. It was decided not to abrade the coupons, as this would increase the reactivity of the metal, or polish, as this may introduce further reactions from residues on the coupons. Four replicates were used for each set of ageing conditions along with four control coupons to allow duplicates to be used in experiments after the accelerated ageing.

To study the effects the display environment has on the deterioration of cellulose nitrate a range of accelerated ageing conditions were chosen. Internal pollutants and dust were not studied as the Centrepiece is on open display. The light ageing conditions were based on the lighting in the dining room at Apsley House, where the Portuguese Centrepiece is displayed. The room is lit primarily by natural light with a maximum of 200 lux, controlled using window blinds. This gives an annual light budget of 0.6 Mlux hours. Ultraviolet (UV) light is blocked using UV absorbing film on the windows, therefore UV was excluded during the ageing. The light box used contains artificial daylight florescent bulbs producing a light intensity of 9000 lux, which is assumed to be constant. Fans in the lid of the light box ensured there was adequate ventilation, also removing any products from the deterioration of the other materials in the light box. The temperature and humidity conditions inside the light box were the same as those in the room (23 ºC and 50%RH). Table 1 shows the range of accelerated ageing conditions used.

In deciding what temperature to perform the hydrolytic accelerated ageing experiments at, it was important that the reactions occurring were those that would occur at room temperature. Above the glass transition temperature (T_g) the polymer can move more freely which may permit other reactions to occur. Initial difficulties in determining the T_g experimentally led to the experiments being carried out based on literature values. The ageing was undertaken at 50 ºC, as the T_g for other cellulose nitrate products are reported to be 53 ºC (Aldrich) and 56 ºC (Conservation Resources). The rate of deterioration at room temperature (20 ºC) and during accelerated ageing (50 ºC) was calculated using the Arrhenius equation, with the activation energy quoted by Selwitz (1988). To simulate likely conditions for objects on display in both Apsley House and general museum environments a range of humidity levels were chosen. These were maintained with saturated salt solutions. The salts chosen were magnesium chloride ($MgCl.6H_2O$) for the low RH (30.5%), sodium nitrate ($NaNO_3$) for the mid RH (57.5%) and sodium chloride (NaCl) for the high RH (74.4%).

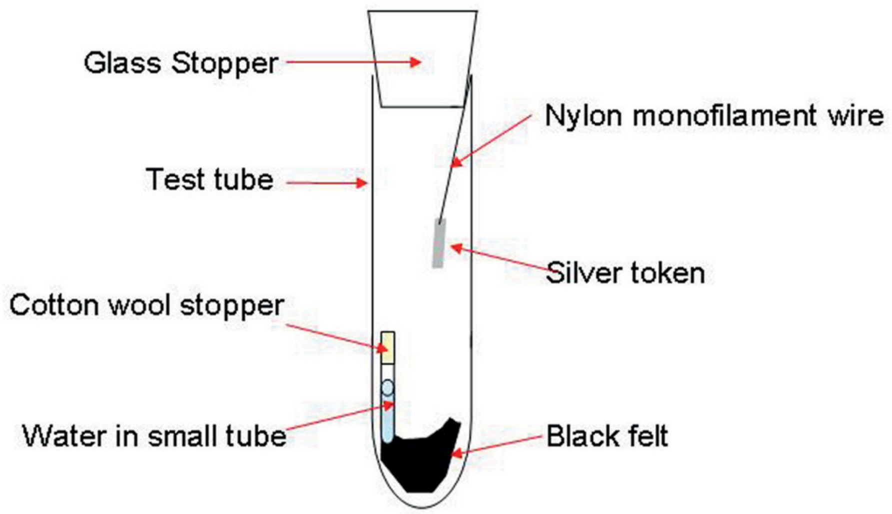

Figure 2: Accelerated tarnish test experimental set up

After completion of the accelerated ageing experiments, the coupons were analysed by FTIR spectroscopy and colorimetry. These give a measure of the changes compared to the control coupons; however this cannot demonstrate whether the lacquer is still preventing silver tarnish. To determine the point of lacquer failure, one of the silver tokens from each ageing experiment was used in an accelerated tarnish test (see figure 2). The test was adapted from the accelerated corrosion test for effects on metals, commonly referred to as the 'Oddy' test (Green and Thickett 1995). It is desirable to further analyse the degree of protection remaining after ageing and electrochemical impedance spectroscopy is underway. To assess the effect of pollutants in Apsley House rather than accelerated tarnishing the aged coupons have been placed in the room with the centrepiece. The protective effect of the aged lacquer is being monitored with colorimetry and the polarisation curve (Costa 2002). In situ FTIR analysis allowed the state of deterioration of the lacquer on the Portuguese Centrepiece to be determined. This allowed comparison of the level of deterioration from ageing under natural display conditions with those from the accelerated ageing experiments.

Results and discussion

Tokens were analysed after accelerated ageing using multiple reflection with a Perkin Elmer 2000 FTIR with AmplifIR. The peak heights of the carbonyl peak at 1716cm^{-1} was compared with the asymmetric nitrate stretching peak at 1644cm^{-1} to analyse the level of deterioration. The nitrate peak does not occur at a fixed wavenumber, but moves between 1644 and 1660cm^{-1} (see figure 3). It is possible this results from the nitrate group being lost from different positions on the cellulose nitrate ring. A background of sterling silver was used for the FT-IR analysis. The accelerated ageing token results were compared with the control coupons. The ratio of the carbonyl to nitrate peak height is calculated and plotted against the time simulated by the accelerated ageing. It is well known that results with high absorbance values, generally above 0.8 can be non-quantitative in FTIR spectroscopy. Therefore two very high results that were obtained have been excluded. The average values of the coupons for each set of conditions are shown in figure 4. Overall the results show a gradual increase in the carbonyl peak compared with the nitrate peak. This is indicative of cellulose nitrate deterioration. The results show that light ageing has caused the most deterioration as measured by FTIR. The

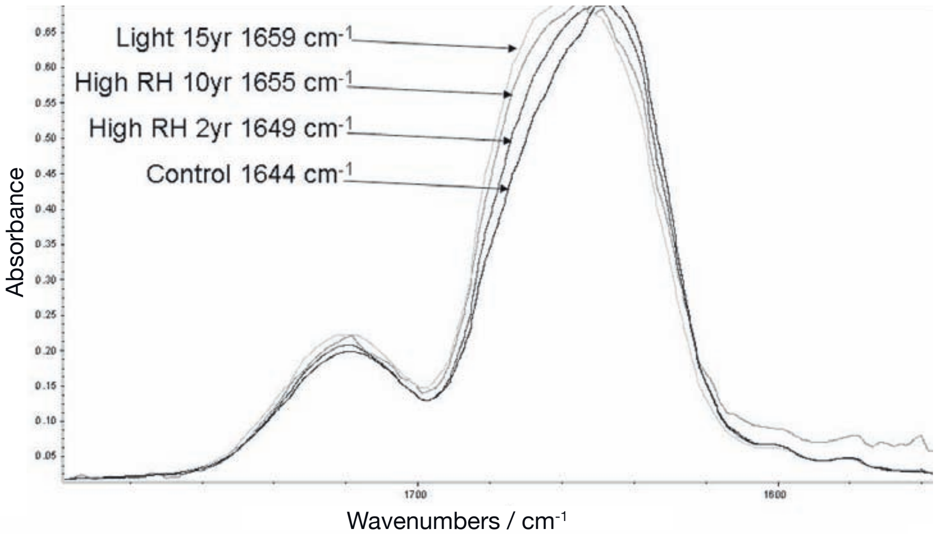

Figure 3: Example of nitrate peak movement in FTIR analysis

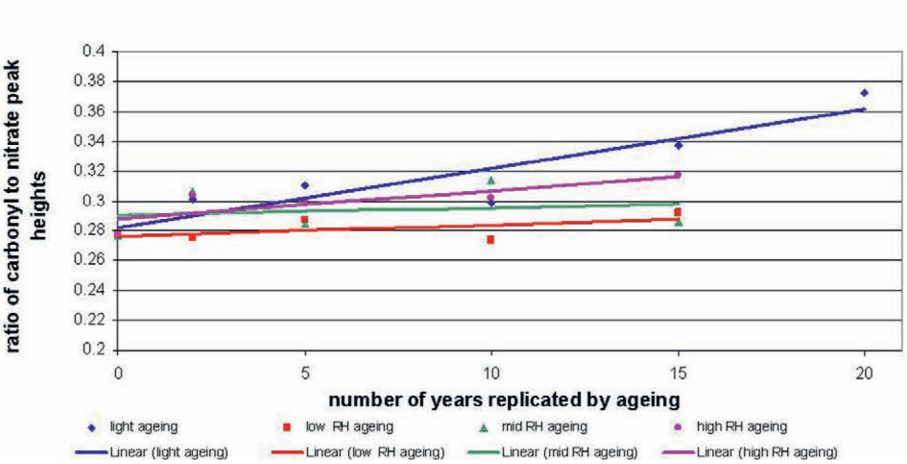

Figure 4: FTIR analysis of accelerated ageing results (trend lines are indicative only)

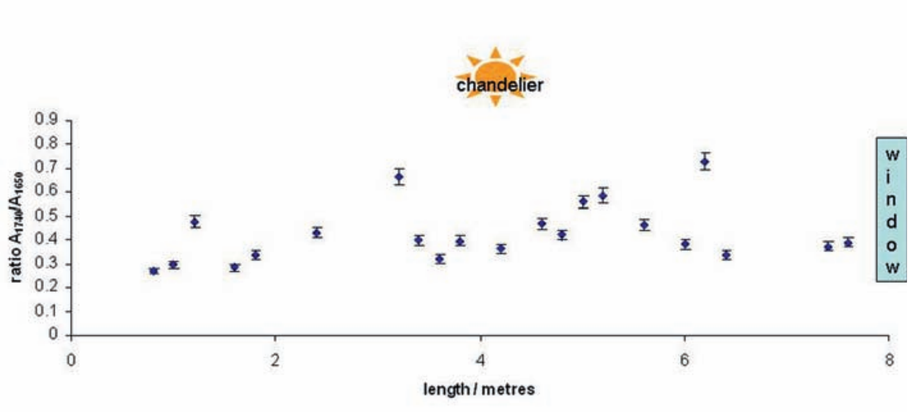

Figure 5: FTIR in situ analysis of Portuguese Centrepiece

hydrolytic and thermal accelerated ageing coupons show a smaller change in the ratio compared with the light accelerated ageing. The least amount of deterioration with ageing is seen for the low RH accelerated ageing. The results show an increase in the deterioration with increasing RH.

The FTIR analysis of the Portuguese Centrepiece showed a range of peak height ratios between 0.13 and 0.73 (see figure 5). The results generally fall between 0.2 and 0.45, the same region as the accelerated ageing results. The higher values (greater than 0.5) occurred on two areas of the Centrepiece. One end of the Centrepiece (6 to 8 metres) is close to the windows, whilst the other end is lit only by the room artificial lighting. There is an increase in the ratio, and therefore the deterioration, towards the window end of the Centrepiece. The accelerated ageing experiments have shown that light causes greater deterioration than the thermal or hydrolytic mechanisms. Therefore greater deterioration would be expected at the window end where light exposure is higher. The other area of higher deterioration occurred around the middle of the Centrepiece (3 to 5 metres). A leak from the ceiling had been reported in this area and the water appears to have deteriorated the cellulose nitrate.

Colour changes on the test coupons were compared with the control coupons, with the colour difference (ΔE_{00}) calculated using the CIE 2000 equation (Luo et al. 2001). The accelerated light ageing shows a decrease in the colour change with increasing time (see figure 6). However the control coupon shows a negative Δb^* upon lacquering, indicating a blueing of the surface. If the control value is subtracted from the other b* values recorded after ageing there is a gradual increase in the b* colour change from blue to yellow. For the thermal and hydrolytic accelerated ageing there is a gradual increase in the colour change with time. The RH also seems to have an effect; with the low RH aged coupons showing the greatest colour increase (see figure 6). The lacquer was removed from one coupon from each set of ageing conditions, using acetone and the colorimetry repeated. Under the lacquer there was a noticeable yellowing on some coupons. For the high RH tokens, the colour change after the lacquer was removed, generally increased with the length of ageing. The colour change measured after the accelerated ageing for the high RH coupons was small. So the increase in the colour change measured after the lacquer was removed, suggests the yellowing was masked by the lacquer. This means colorimetry may not be suitable for measuring colour changes on lacquered silver. As colour changes may be occurring beneath the lacquer that are not recorded by the colorimeter.

In the accelerated tarnish test one coupon from each artificial light aged time period was run. For the thermal and hydrolytic accelerated ageing, coupons from the 2, 5 and 10 year simulated time periods were tested. Green corrosion (see figure 7) was observed on some coupons after high RH accelerated ageing, possibly after touching the side of the container. The high 10 year coupon had visible dark spots of tarnish, close to the corrosion. This suggests the lacquer is no longer protecting against tarnish. The FTIR results for this token showed less cellulose

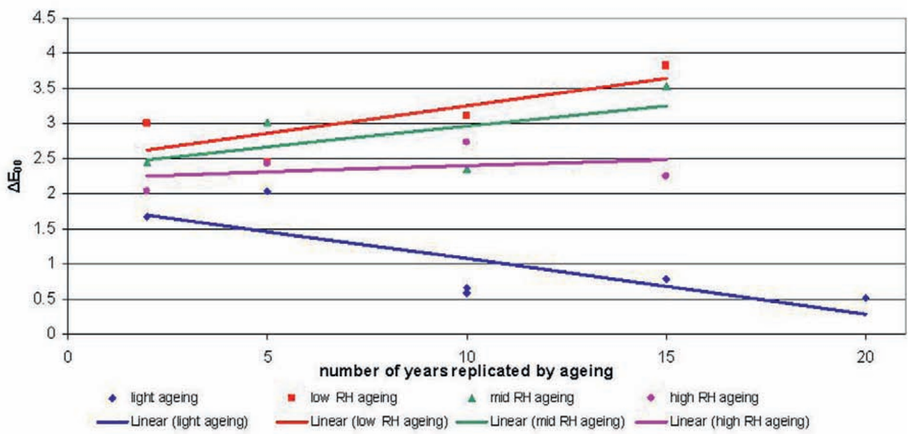

Figure 6: Colorimetric analysis of accelerated ageing results, calculated using difference between aged samples with controls therefore results start at 2 years (trend lines are indicative only)

nitrate lacquer deterioration than the light accelerated ageing tests which had been aged for longer. However the light accelerated ageing tokens had no noticeable corrosion. For the light aged coupons the accelerated tarnish tests have shown the lacquer is still protective after the equivalent of 20 years accelerated ageing. The tarnish tests have shown cellulose nitrate to be protective against silver tarnish after the equivalent of 10 years accelerated ageing in low and mid RH environments. This figure is likely to be an underestimate of the length of time silver is protected by cellulose nitrate lacquer coatings. Longer equivalent ageing period coupons are presently undergoing accelerated tarnish tests to determine their effectiveness.

Conclusion

Accelerated ageing tests of the lacquer have shown light has the most pronounced effect, with high RHs causing the next greatest amount of deterioration. These results have been confirmed with the in-situ FTIR deterioration analyses.

Accelerated tarnish tests demonstrated the lacquer was still effective in protecting against silver tarnish after the equivalent of 20 years light ageing. It was also shown to be effective after at least 10 years ageing in low and mid RH environments, however accelerated tarnish tests were only undertaken up to ten years RH ageing. Since the heat and RH ageing had less deteriorating effect, it is highly likely that the thermal and hydrolytic lifetime in the centrepiece environment is in excess of twenty years. This predicts another eight years effective lifetime for most of the lacquer on the centrepiece. The areas that were exposed to liquid water from the roof leak are more deteriorated and local replacement will soon be required. Much higher RH environments have been shown to cause corrosion and tarnishing of sterling silver coupons aged for the equivalent of 10 years at ambient temperatures. The validated ageing tests have informed the environmental regime for the room containing the Centrepiece.

Figure 7: Example of green corrosion on high RH aged coupon

Acknowledgements

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Materials list

- Sterling silver

West Dean College
West Dean, Chichester
West Sussex, PO18 0QZ, UK
Tel +44 (0) 1243 811301

- Saturated Salts

VWR International Ltd.
R&L Slaughter Ltd
Units 11 & 12, Upminster Trading Park
Warley Street, Upminster
Essex, RM14 3PJ, UK
Tel +44 (0) 1708 227140

- Frigilene T65150,

W. Cannings Materials Ltd.
Great Hampton Street.
Birmingham, B18 6AS, UK
Tel +44 (0)121 2368621

- Light box with twelve F20W/AD artificial daylight, fluorescent bulbs, UV filter and four SUNON SF23092A fans, (Made especially for the V&A), Complete Lighting Systems

Harper Lodge Farm
Harper Lane, Radlett
St. Albans
Hertfordshire, WD7 7HU, UK
Tel +44 (0)1923 859988

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