Study on the light fading of iron gall inks on parchment

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Abstract

This ongoing study looks at the effect of a specific display lighting system on the fading of iron gall inks on parchments. Light-aging equipment incorporating non-UV tungsten halogen and fluorescent lighting has been developed to create accelerated lighting conditions based on those used in the National Archives of Australia's Federation Gallery, where items of great importance to Australia's cultural and political heritage are on permanent display.

Handwritten samples taken from English indenture documents of the 19th and 20th centuries are being used, as well as inks prepared to various compositions and traditional recipes. Any fading or colour changes in the ink samples are being monitored by reflectance spectrophotometry. This paper presents the development and theory behind the light-aging experiments and light-aging device construction, and does not report results as the experiments are in progress.

Introduction

Iron gall inks were used extensively from the late Middle Ages until the early part of last century. Libraries, archives and cultural institutions around the world now hold collections of historic iron gall ink documents, manuscripts and artworks on paper and parchment supports. These range from everyday letters and indenture documents to medieval illuminated manuscripts, musical compositions by J S Bach and sketches by Rembrandt and Van Gogh.

Many iron gall inks have a corrosive nature and a tendency to undergo colour change from black to brown, often fading quite significantly. Whilst many historic documents, manuscripts and artworks remain in excellent condition, certain combinations of environmental storage conditions and the composition of the ink and/or support have and will in many cases result in lightening of the ink and losses due to the ink effectively 'eating' its way through the support or flaking away.

Iron gall inks on parchment supports were used almost exclusively for federation documents (c.1900) of great importance to Australia's cultural and political heritage held in the collection of the National Archives of Australia (NAA). Queen Victoria's Commission of Assent to the Commonwealth of Australia Constitution Act, 9 July 1900 (Figure 1a) was written in England by a scribe with iron gall ink on a parchment/vellum support, and signed in iron gall ink by Queen Victoria at Windsor Castle. The Queen signed two content-identical documents that day, giving legal consent for the creation of the Commonwealth of Australia and enacting the Australian Constitution. The visually impressive 'display' copy was presented to Edmund Barton, Australia's then Prime Minister, along with

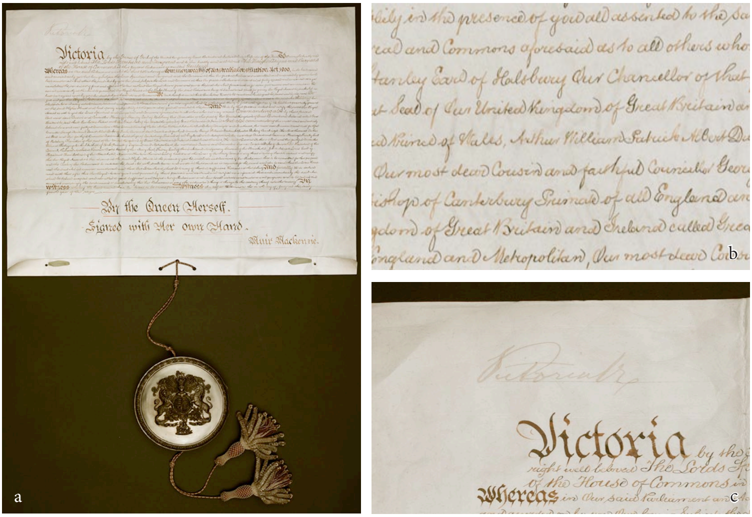

Figure 1. Queen Victoria's Commission of Assent to the Commonwealth of Australia Constitution Act, 9 July 1900, National Archives of Australia [NAA: A5137]. a) full recto b) main body of text [central detail] c) Queen Victoria's signature [top left detail].

the table, pen and inkwell used, and brought out to Australia soon after the signing. For decades it was displayed at Old Parliament House under varying, unregulated environmental conditions, including natural light. The NAA became custodian of the Royal Assent in 1988. Since 2001 it has been on public display in the NAA's Federation Gallery under strict preservation conditions, along with a number of other related federation documents. Visual examination shows it has been overwritten in a number of locations (Figure 1b), with possibly a number of different inks. The use of iron gall ink for both the original and overwriting inks was confirmed by C Whitley in 2003, using non-destructive bathophenanthroline iron(II) indicator strips developed by the Netherlands Institute for Cultural Heritage (Neevel and Reissland 2005). Records of these overwritings, if they exist, have not been found, but the overwriting was most likely done prior to 1940, based on photographs from that time. However it can be seen clearly that Queen Victoria's signature in the top left corner has, for obvious reasons, not been overwritten (Figure 1c). It is now a very pale brown colour, as is most of the original writing. The original and overwriting inks have undoubtedly undergone fading and colour change during the document's lifetime, and our concern is with preventing any future light-induced fading.

Light-induced fading or colour change of a material is a form of photochemical damage caused by the absorption of light energy and subsequent alteration of the molecular structure of a light-sensitive material (Miller and Miller 2003). It is considered one of the most serious threats to the preservation of an object, particularly when the content or purpose of the object is endangered, such as the writing on a document becoming too faded to read.

It is commonly known that sunlight, particularly sunlight with no UV filtering, is the most damaging form of light for objects. Most museums and galleries now employ strict, monitored preservation conditions for objects on display, with low-lux-level artificial lighting that has no (or a filtered-out) UV component. Although the process is slowed, some light-sensitive materials still fade in typical display lighting, which might use light from sources including IR-filtered, dimmed or full-voltage incandescent lamps and UV-filtered fluorescent lamps (Miller and Miller 2003).

The aim of this study is to determine if the Federation Gallery's current display lighting will cause light fading of various iron-gall-inked parchment documents, and if so, in what approximate time frame. The relative effects of different iron gall ink compositions, including excess of particular ingredients, additional compounds or dyes, are of interest if fading or colour changes do occur. The results of these light-aging experiments will be used to establish long-term display lighting parameters for the Federation documents.

Iron gall ink chemistry

Numerous recipes and ingredient sources were used to make iron gall inks, resulting in differing compositions and component proportions. The ink is essentially made by the combination of iron(II) sulfate with tannins (tannic or gallic acids either from plant gall extract or, in later years, as pure compounds) in various proportions. These ingredients were combined in water, with the tannins breaking down to gallic or di-gallic acids to give rise to the oxidized black ink complex believed to be iron(III)–gallic acid or iron(III)–pyrogallin (Krekel 1999; Wunderlich 1994) with sulfuric acid as a by-product. Gum arabic was usually added to provide fluid writing properties and keep the ink particles in suspension. Historic recipes record various preparative methods, including boiling and/or fermenting the mixture. Other compounds and dyes were sometimes added to alter tone, provide immediate visibility or adjust physical properties of the ink. Hence, a number of historic inks and prepared inks of various compositions are being used in these light-aging experiments.

Many historic iron gall ink inscriptions remain black, but some have become varying shades of brown over time. This brown colour is not necessarily due to light deterioration but rather due to complex oxidation, hydrolysis or polymerisation processes resulting in brown degradation products: a mixture of phenol products, various oxides of iron or even cellulose or protein/collagen oxidation products of the paper or parchment support (Krekel 1999). Additionally, it is likely that some inks, particularly prior to the 17th century, were brown to start with, e.g. if a high proportion of iron(III) salts rather than iron(II) salts were used, or a higher-acidity ink was prepared (Krekel 1999). Given the purpose and date of the Royal Assent, it is unlikely the ink was originally brown. The reasons for the inks of the Royal Assent being brown are not the subject of the study reported here. The document is believed to have faded over the years of previous display and the present concern is whether or not its current lighting will cause further fading.

Previous accelerated light-aging studies on laboratory-synthesized iron gall inks on paper have indicated that iron gall inks are sensitive to lamps simulating 'daylight through glass', i.e. containing a 320–380 nm UV component (Reissland and Cowan 2002).

Light-induced fading and colour change

Fading or colour change induced by light is a photochemical deterioration process. The Grotthus–Draper Law is a key principle of photochemical phenomena; only radiation that is absorbed by a substance may cause a chemical reaction (Feller 1994). Light is a form of radiation, delivered as photons ('packets' of energy). Each wavelength of light in the electromagnetic spectrum has a certain amount of energy (from higher energy, shorter ultraviolet (UV) wavelengths through the visible region to the lower energy, longer infrared (IR) wavelengths). The Stark Einstein principle states (Feller 1994) that a molecule can only absorb radiation in terms of a discrete quanta of energy (photons of certain wavelengths) and this is dictated by the chemical bonds present in the material; it is therefore material-specific. As a result, a material does not respond equally to all wavelengths, and a given wavelength does not interact with all materials in the same way (Saunders and Kirby 2001).

When a photon is absorbed by a molecule, the energy supplied is said to excite its electronic system. The excited molecule may then lose the absorbed energy by a *photophysical* process (releasing the radiant energy as heat or fluorescence/phosphorescence), or by various *photochemical* processes (undergoing a chemical change within the molecule, breaking chemical bonds (photolysis) or transfering energy to another atom or molecule which may then initiate chemical changes or photolysis) (Feller 1994). With photochemical processes, fading or colour change of the material may be a result.

Wunderlich (1994) suggested that photochemical degradation of the iron gall ink complex is due to the absorption of a photon that will sometimes induce the permanent formation of a gallate radical. This radical may then react with an oxygen molecule from the air destroying the black ink complex and resulting in fading of the ink.

Every light source has a specific *spectral distribution*; the intensity of emitted light at each wavelength of light (UV through visible and IR). A light source therefore delivers certain wavelengths of specific intensity. A material will not respond equally to light sources with different spectral distributions and a given light source will not fade all materials in the same way. This was shown in a collaborative, comparative experiment in which the same range of materials were aged by nine different accelerated light-aging regimes across six cultural institutions in the UK and Netherlands (Saunders and Kirby 2001).

Samples of pigments and materials exposed to light sources containing a UV component (high energy) show either an increased or a similar degree of colour change as those where UV light was excluded (Saunders and Kirby 2001). Complete elimination of UV and IR has been found to decrease the risk of photochemical damage by an average factor of 3–6 (Miller and Miller 2003).

Federation Gallery conditions

The Federation Gallery is part of the exhibition space in the NAA's public-access building in Parkes, Canberra. The relative humidity in the gallery is 40–45% (± 5%), maintained inside display cases by pre-conditioned ProSorb silica gel. The temperature is regulated at 20°C (± 2°C).

The lighting system used in the Federation Gallery is operational between 8 am and 5 pm six days a week and Tuesdays 8 am to 9 pm. The documents are otherwise in the dark. They are each contained in separate security display cases made with 10 mm laminated glass and are illuminated with two different light sources.

The documents each have one 20-watt, 12-volt Osram Decostar Titan tungsten halogen lamp (an MR16 dichroic reflector lamp) directed onto them from the ceiling. These lights are visitor-activated by motion sensors in the gallery for between one and a half to two hours a day on average. The tungsten halogen lights are dimmed from their full intensity to illuminate the majority of the text of the Royal Assent at 20 lux (Queen Victoria's

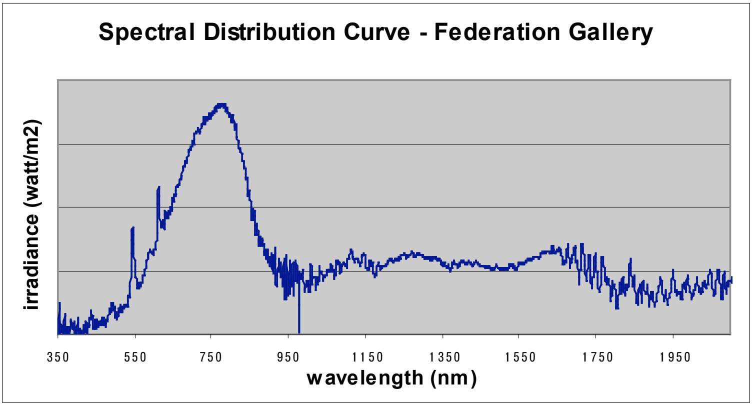

Figure 2. Spectral distribution curve of the light on the documents in the Federation Gallery.

signature is illuminated at 9 lux). The spectral distribution of light from a tungsten halogen (incandescent) lamp is continuous and closely follows a blackbody distribution. They typically emit four times as much red as blue light and have over 90% of their energy emission in the IR (Miller and Miller 2003). The Osram lamps used in the gallery have dichroic reflectors that cut down the IR emission significantly. Additionally, dimming incandescent lamps moves the spectral distribution toward the red and infrared, indicated by a decrease in colour temperature. The lamps in the gallery have a colour temperature of around 2020 K.

Sylvania T8 Luxline Plus, 840 Coolwhite Deluxe fluorescent light tubes also illuminate the gallery at low levels from behind a frosted glass panel on a side wall the entire time the lighting system is operational. As a consequence the documents receive 5 lux of light from this fluorescent lighting. A fluorescent lamp is a low-pressure gas discharge lamp whose spectral distribution consists largely of discrete lines in the UV and visible (blending to give 'white' light) from mercury electronic transitions and the solid phosphor coating (Miller and Miller 2003). By differing phosphor compositions different spectral distributions are achieved, and therefore fluorescent bulbs are marketed according to the 'tone' of white light they produce.

The individual and combined spectral distributions of the two light sources in the Federation Gallery were measured in terms of irradiance at the document, using an Analytical Spectral Devices (ASD) FieldSpec Pro Full Range spectroradiometer over 350–2200 nm. It shows the superimposed tungsten halogen and fluorescent components for the UV through IR (Figure 2). The glass of the cabinet and frosted-glass side wall do not have a large effect on the distribution, but nonetheless accelerated aging tests are being conducted with and without the glass.

The NoUVIR group in the USA, who promote the absence of both UV and IR components in exhibition lighting, has found that despite having no UV component, MR-16 halogen lamps with dichroic reflectors did cause some fading (around 50% of solar fading after 250,000 footcandle-hours) of ISO Blue Wool samples #1–3. However, the heat produced by the lamps was not regulated to museum conditions in these tests (Miller and Miller 2003).

Development of light-aging devices

Accelerated light aging is based on the reciprocity principle: the amount of damage caused by a given light exposure is independent of the time over which that exposure is delivered (Feller 1994). For example, the same amount of damage should result from exposure to 100 lux for 10 hours as from exposure to 10 lux for 100 hours (cumulative exposure of 1,000 lux hours). This theory was confirmed on a number of light-sensitive materials by Saunders and Kirby (1996).

Galleries and museums testing the light aging of materials for conservation purposes use both commercially available and 'in-house' constructions (Saunders and Kirby 2001; Whitmore et al. 1999). Since our aim is to light age samples using specific lighting conditions, it was necessary to design and construct light-aging equipment for our purpose. Separate devices for the two light sources will enable any differences in the effect of each to be seen.

In designing the equipment our objective was to obtain the maximum lux levels from the light sources whilst keeping within the gallery temperature and relative humidity ranges. This was required in order to achieve light aging in reasonable time periods and to minimise any

Figure 3. Light-aging devices: a) tungsten halogen component, b) fluorescent component.

non-light-induced fading or colour change (e.g. from heat and moisture). Constant temperature and relative humidity were achieved by locating the equipment in an air-conditioned room and experimenting with sample distance from the light sources. The use of fans was not necessary at the distances chosen. Simplicity, low cost and ease of construction were also design considerations.

For the tungsten halogen component, the 50-watt model of the same Osram Decostar Titan lamp type (same materials and dichroic filter) was chosen as the light source, to match the spectral distribution with maximum lux intensity. The lamps are dimmed to the same colour temperature as those in the gallery so the shift in spectral distribution is matched. The light-aging device for this light source has been constructed as a track lighting system with individual electronic transformer heads for four tungsten halogen lamps and an overall dimming system (Figure 3a). The 1 m track is supported at either end so that the lights are 25 cm above a tabletop and samples lay flat under each circular area of around 1,200 lux illuminance.

A Sylvania Compact Fluorescent Mini Lynx 18-watt, ES 840 lamp was chosen as the fluorescent light source. Manufactured by the same company with the same materials, the '840' specification (named Coolwhite Deluxe) indicates that it has the same spectral distribution as the standard long fluorescent tube used in the gallery but it is in a more practical compact form for the device. The lamp is mounted on a wooden board base with a stainless steel cylinder (40 cm diameter) surrounding it (Figure 3b). Samples are suspended along the walls of the cylinder in selected areas with an illuminance of 4,200 lux.

Samples and exposure

The experiments use common, purchased, non-collection 19th- and 20th-century English indenture documents written in iron gall inks on parchment sheets along with many laboratory-prepared representative iron gall inks on parchments. The purchased documents are from a similar time period as the federation documents. This aims to give a general idea of iron gall ink fading under the gallery's lighting conditions since the ink composition of the Royal Assent and related federation documents is unknown. It is anticipated that the responses of the newly prepared and historic inks may be different as photochemical deterioration is not necessarily constant over time, and is likely to be influenced by natural aging and/or the amount of fading that has already occurred.

The smallest target mask available for the spectrophotometer has a 7 mm circular diameter hole that uses a 4 mm circular diameter measurement area. This is larger than the area of even the bold ink lines in the historic documents. Consequently, the historic samples have been prepared by adjacently attaching many thin strips of ink lines cut from throughout the given document to a support. The measured changes for fading and colour will be an average of the change in the strips as a whole, which is useful in indicating how the overall document would behave. The laboratory-prepared, known-composition inks (prepared to traditional recipes or varying compositions) were each applied as an approximately 1 cm diameter solid circle onto approximately 2 cm × 4 cm pieces of traditionally prepared parchments from Pergamena (US) and William Crowley (England). The inks were left to dry and stabilise for at least a month, whilst some had been applied three years prior to this study. Three samples of each prepared ink type and historic document are being used in order to better approximate real trends in fading or colour change.

Light meters commonly used to measure lux levels respond to a range of wavelengths centered in the visible at 560 nm, and do not reflect the total radiation (UV and IR) delivered to the sample (Saunders and Kirby 2001). However, the use of light sources with identical spectral distributions allows intensity comparisons between the gallery and aging device to calculate the acceleration factor; i.e. equivalent 'gallery time' of the aging device exposure.

Based on the 12 hours per week of tungsten halogen and 67 hours per week fluorescence lighting received by the documents in the gallery, the increase in lux levels in the aging devices mean that one year's lighting in the Federation Gallery is achieved by approximately 10.4 hours of exposure in the tungsten halogen light-aging device and approximately 4.15 hours of exposure in the fluorescent light-aging device. Small variations in lux levels of the aging devices are recorded and accounted for by altering length of exposure. The samples are being exposed in the light-aging devices for accumulating time periods approximating 1, 5, 10, 20, 50, 75 and 100 Federation Gallery years.

Spectrophotometry and colour measurements

Spectrophotometry is a non-invasive technique used to measure the amount of light reflected or transmitted by a material at individual wavelengths of the spectrum (Johnston-Feller 2001). By combining this analytical method with the widely accepted colorimetric CIE L*a*b* system developed by the CIE (Commission Internationale de l'Eclairage), the colour can be described numerically in terms of three dimensions: L (lightness), a (+ redness – greenness), and b (+ yellowness – blueness). ΔE* is calculated to represent the total colour difference between two samples, or in this case, before and after light exposure, and is given by $\Delta E^*_{ab} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$ (Johnston-Feller 2001; Saunders and Kirby 2001). A colour change of $\Delta E^*_{ab} = 1.7$ is considered 'just perceptible' by the naked eye (Reissland and Cowan 2002).

Any changes in colour and fading of the samples due to light exposure in these experiments are being monitored by colour measurements taken initially and after each light exposure period with a Minolta Spectrophotometer CM-3600d in reflectance mode.

Each sample has its own white Reflex paper fixed masking with a standard 'hole punch' (just smaller than the 7 mm target mask) to allow us to line up and reveal the same part of the sample for light-aging exposure and presentation to the spectrophotometer each time. The Reflex paper has been aged and tested, showing negligible changes in colour parameters under these light-aging conditions. To statistically improve the accuracy of colour measurements, five readings are being averaged for each sample after each exposure period and the sample is removed and repositioned between measurements.

Since the historical ink compositions are unknown and of varying ink layer thicknesses and shades, the objective in this case is to simply see whether fading occurs or not. The known composition of prepared ink samples will allow experimental comparisons between different ink compositions prepared at the same time.

SpectraMagic control software interfaced to the spectrophotometer presents data in the selected CIE L*a*b* colorimetric system in addition to the graphical presentation of per cent reflectance versus wavelength in the 360–740 nm range. Trends in L, a, b and ΔE values will be examined. In order to report only true changes and trends in colour-change measurements, the results of these experiments will be published on completion of the study.

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References

Feller, R. L. 1994. *Accelerated aging: Photochemical and thermal aspects.* Los Angeles, California: Getty Conservation Institute

Johnston-Feller, R. 2001. *Color science in the examination of museum objects: Nondestructive procedures.* Los Angeles, California: Getty Conservation Institute

Krekel, C. 1999. The chemistry of historical iron gall inks. *International Journal of Forensic Document Examiners* 5: 54–58

Miller, R. E., and J. V. Miller. 2003. *Reflected energy matching as a conservation tool.* Seaford, Delaware: NoUVIR Research Institute

Neevel, J. G., and B. Reissland. 2005. Bathophenanthroline indicator paper. *Papier Restaurierung* 6 (1): 28–36

Reissland, B., and M.W. Cowan. 2002. The light sensitivity of iron gall inks. IIC Baltimore Congress, Baltimore: IIC. 180–184

Saunders, D., and J. Kirby. 1996. Light-induced damage: Investigating the reciprocity principle. ICOM-CC 11th Triennial Meeting, Edinburgh: James & James. 87–90

Saunders, D., and J. Kirby. 2001. A comparison of light-accelerated aging regimes in some galleries and museums. *The Conservator* 25: 95–103

Whitmore, P. M., X. Pan, and C. Bailie. 1999. Predicting the fading of objects: Identification of fugitive colorants through direct nondestructive lightfastness measurements. *JAIC* 38 (3): 395

Wunderlich, C. H. 1994. Geschichte und chemie der eisengallustinte. *Restauro* 100: 414–421

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