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The light-fastness of textiles dyed with 6,6′-dibromoindigotin (Tyrian purple)

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Abstract

The colourant in the ancient dyestuff Tyrian purple is predominantly 6,6′-dibromoindigotin. The light-fastness of a synthetic version of this dye was investigated by dyeing six different textile types and subsequently performing accelerated light fading. The hue of the samples were measured using the CIELab system and fading rate constants derived for each sample. A range of samples of different initial shades of dyeing were obtained so that, for each fibre type, characteristic curves could be obtained showing the way initial depth of shade of dyeing varies the fading rate. All dyed textiles were most light-fast at deeper shades. Of the various textile types, dyed wool was most light-fast followed by silk, linen, nylons 6 and 66 and finally cotton.

Keywords: Tyrian purple; Indigoid; Fading; Textile; Dye

1. Introduction

The dyestuff known as Tyrian purple has as its principal component 6,6′-dibromoindigotin. The dye is obtained from the hypobranchial gland in certain molluscs. The gland yields precursors which eventually produce a purple substance which can be used to dye a wide range of fibre types. In the last 10 years there have been tremendous advances in our understanding of the dye and we now know that a range of molluscs, ranging in origin from Scotland to South America yield the dye and that the mixture of compounds that can be obtained can contain unsubstituted, mono- and dibrominated indigotins and indirubins [1–3]. Modern methods of analysis such as high performance liquid chromatography with diode array detection have been used to elucidate the chemistry of the dye [4–6]. A comprehensive bibliography on Tyrian purple was published in 1994 and an up-to-date version of this is available electronically [7].

The light-fastness of dyes on dyed textiles in museum collections is a matter of great concern for conservators and it is often seen that textiles in museum galleries are on display for limited amounts of time, thus reducing the total exposure to light considerably. Often the light has also had its illuminance and ultraviolet content reduced [8]; although this is good for the preservation of the textiles the visibility of the objects can be impaired due to the low light levels. Textiles dyed with Tyrian purple were of the highest quality and relatively few were made. Thus, it is important to know as much as possible about the response of the dye to light in order to devise conservation strategies for these scarce objects.

As part of a project on the properties of indigoid dyes, the light-fastness of indigo-dyed textiles has been recently investigated [9]. As indigo and dibromoindigotin are chemically related the fading properties of one of these dyes might be reflected in the properties for the other. It was discovered that the sensitivity of indigo to light was influenced strongly by both the initial depth of shade and the textile substrate. This is in line with the findings of previous researchers such as Giles and McKay who found that the rate of fading decreased with the increasing concentration of dye on the fibre [10]. Giles proposed that “characteristic fading curves”, which were graphs of sensitivity to light against the initial concentration of dye, gave a better picture of the light-fastness of dyes than a single light-fastness obtained for a typically dyed sample.

It has been reported [11] that the fading rate of indigo depends on the fibre type it is dyed onto. The fading rate of indigo on

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cotton is known to be higher than on wool and thus it was assumed, by extrapolation to other fibres of the same chemical type, that the fading rate of indigo would be higher on all cellulosic materials than on all proteinaceous materials. However, the research on indigo [9] showed that at all depths of shade, rates of fading were similar on cotton and silk which were in turn higher than the rates on wool and linen.

The rate constants for the fading of blue wool standards and the indigo-dyed textiles have been obtained previously [9]. Comparison of the results showed that compared with blue wool (BW) standards the indigo-dyed cotton and silk had light-fastness corresponding to BW 2 (palest shades) and at least 6 (deepest shades) while wool and linen were between BW 4 and 5 (palest shades) and at least 6 (deepest shades).

While several workers have reported results on the light-fastness of indigo-dyed textiles [12,13] and additional anecdotal evidence exists, ideas and data on the light-fastness of dibromoindigotin (DBI) dyed textiles are very few reflecting its rare occurrence and negligible commercial importance. The synthetic dye is still extremely expensive and uncommon. The only available data on light-fastness of DBI comes from Hofenk de Graaf who reports that the light-fastness of DBI on textiles corresponds to blue wool standard 7–8 depending on the method of dyeing [14]. The light-fastness was reported to be “comparable to that of indigo”.

Indigo and DBI are unusual dyes because, in the solid state, they can be dispersed in a binder and used as a pigment. The state of knowledge regarding the light-fastness of these indigoid pigments is less than for the dyed textiles. Indigo pigment was commonly used by artists up to about the 1930s but is no longer available from the major artists’ suppliers on account of its alleged high fading rate [11,12]. Indigo was widely used as a pigment both in oil and in water-based binders but DBI as a pigment has only been found on a few museum objects and there is no published information on its light-fastness.

Encouraged by the significant differences found with the light-fastness of indigo dyed onto wool, silk, cotton and linen, it was decided to investigate the light-fastness of DBI on the same substrates and over a range of depths of shade. However, for DBI, two additional substrates were used, namely nylon 6 and nylon 66. These two synthetic substrates were included because the colour of DBI dyed onto them is significantly different from the hue on natural fibres. This might be because the state of aggregation or the bonding to the fibre was significantly different. Cooksey and Sinclair [5], report the hues produced on six textiles in a multi-fibre strip ranged from moderate reddish-purple on wool to moderate violet on nylon 66. The difference in hue was attributed to a range of factors including the amount of crystallinity in the various fibres but the principal reason quoted was the affinity of the fibre for DBI. In nylon the dye is considered to be able to retain the absorbed leuco dye on the fibre during the oxidation process but in wool the leuco dye more easily migrates and forms intermolecular aggregates.

The numbering for nylon nomenclature is as follows. Many nylons are made by the condensation of amines with acids. Water is split off with the formation of polymer chains. In nylon 66 the first number is the number of carbon atoms in the diamine, the second number is the number of carbon atoms in the acid. Thus, nylon 66 is made from hexamethylene diamine $H_2N(CH_2)_6NH_2$ and adipic acid $HOOC(CH_2)_4COOH$. Nylon 6 is made of caprolactam a cyclic molecule with six carbon atoms and internally linked amide which self-polymerises to form the polymer.

2. Experimental/materials and methods

2.1. Materials

Synthetic DBI was kindly provided for this work by Professor Peter Imming. The product was at least 90% pure and contained no indigotin. Nylon samples were from an educational kit of textiles supplied by British Drug Houses and the other textiles were from Whaleys (Bradford) Ltd. who were able to provide textiles free of finishes. The silk was supplied degummed.

2.2. Dyeing method

Prior to dyeing, textiles were washed in a mixture of water with 1% of an ionic surfactant (Hostapon T) at 60 °C for 10 min. Subsequently the textiles were washed in flowing cold water for 60 min. Usually dyeings with indigoid dyes are carried out in an open vat but due to the small amounts of ingredients used, the surface area of solution was high compared to the volume of liquid. This raised the possibility that effective reduction of the DBI might not occur; thus a sealed vessel in which the oxygen content of the air might be depleted during the dyeing was used. Each dyeing was carried out in a 1 l glass jar with an air-tight lid.

The basic dyeing recipe was taken from Böhmer for dyeing with indigo however the quantity of DBI used was varied to change the depth of shade obtained [16]. The dye vat, usually 150 ml, contained gelatine (0.2%), sodium hydroxide (0.1%) sodium hydrosulphite (0.5%) and DBI (0.05–0.1%). The percentages are real percentages in solution rather than being based on the mass of the textile to be dyed. The glass jar, which formed the dye vat, was maintained at approximately 60 °C in a water bath. The lid was sealed to make the jar air-tight and the jar shaken occasionally until all the dye had been reduced and an orange solution was obtained. Pieces of cloth to be dyed measured approximately 10 cm × 10 cm. All six types of fibre were dyed simultaneously and had a combined mass of approximately 12 g (silk 0.5 g, wool 1.8 g, cotton 1.8 g, linen 2.6 g, nylon 6 2.5 g and nylon 66 2.5 g) Textile samples, still damp from washing, were placed in the fully reduced dye and left there for 5 min before removing and rinsing in cold water. The textiles were left for an hour to develop their full colour and then washed for 2 h in flowing cold water. It is not considered that there was competition between the fibre types for the available dye as there was sufficient dye left in solution at the end of the process to produce another batch of dyed textile at only slightly reduced depth of shade.

It is possible for the reduced DBI to be photodebrominated when exposed to strong light. However, Voss [17] used a 250 W mercury lamp for two hours to debrominate solutions of leuco–DBI. The laboratory dyeings described here were performed under the ambient lighting of the fume cupboard which was approximately 250 lx with ultraviolet content under 50 μW/lm (below the measurable levels of the apparatus available). Because sealed containers were used for the dyeing the reduced state of the dye could be maintained for several weeks. Dyeings (not used in the experiments described here) were produced after the jars had been standing in ambient light for 4 weeks, no change in hue could be detected by eye in the resulting dyed textiles. It is therefore, assumed that a negligible degree of photodebromination takes place during the normal dyeing process.

2.3. Fading method

Square pieces of dyed textile for fading, approximately 20 mm × 20 mm, were adhered to a circular piece of white card by their corners only. The piece of card was placed, textile samples side uppermost, in the glass lid of an air-tight glass jar. The interior of the container was maintained at a relative humidity (RH) of 50% by a small volume of 80% (w/w) glycerol/water mixture which gives a RH of 50% from 20 to 60 °C [18]. The jars were placed on the base of a Microscal light-fastness tester with a Philips ML lamp which is a daylight simulation lamp. The illuminance *under* the glass lid, where the samples were, was measured to be 8.0 klx with 400 μW/lm of ultraviolet light. The heat from the lamp elevated the temperature of the samples which could reach 50 °C, depending on ambient temperature. The colour of the samples on their card supports was regularly measured using a Minolta CR-200 tristimulus colorimeter.

3. Calculation

The colour of the samples was measured using the CIE 1976 $L^*a^*b^*$ system [19] in which each colour is represented by three numbers L^*, a^* and b^*. In this system L^* represents lightness, a^* redness if positive and greenness if negative and b^* yellowness if positive and blueness if negative. The difference between colours (ΔE) is given by:

$$\Delta E = \sqrt{((L_1^* - L_2^*)^2 + (a_1^* - a_2^*)^2 + (b_1^* - b_2^*)^2)}$$

It was decided to study the perceived rate of fading by assuming the colour of the undyed textile was the same as the fully faded textile and all ΔEs were measured relative to undyed textile, i.e. the value of ΔE falls as the fading proceeds until, (if all the dye fades to a completely colourless material) the value of ΔE is zero. A typical graph of $\log_{10} \Delta E$ against time is shown in Fig. 1. Here it can be seen that the kinetics of fading are exponential, i.e. first order. Note that changes in visual appearance as measured by ΔE are not necessarily caused by a change in a proportionate amount of dye and that coloured intermediates and final decomposition products may be coloured.

Similar analyses have been performed in the past to study the rate of fading of natural colourants. For example, Whitmore and Bailie [20] plotted the logarithm of reflectance against cumulative exposure to light to obtain rate constants for the fading of translucent glazes. Giles et al. [16] studied the half-life of dye fading in a textile to obtain information on how the fading rate changed with initial concentration of dye.

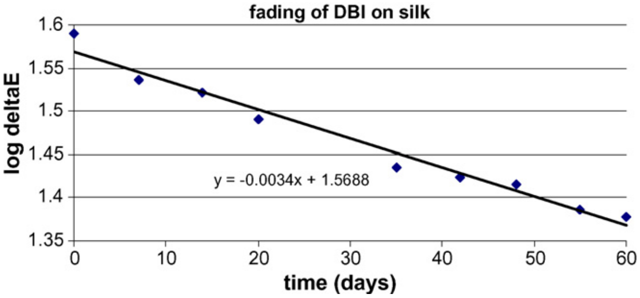

Fig. 1. The fading of DBI-dyed silk.

Rate constants for fading were obtained from graphs of $\log_{10} \Delta E$ against time. The fading rate constants are for visual fading and thus not identical to the rate constant that might be obtained if concentration of DBI were used instead of ΔE. To keep this distinction the experimental rate constants will be referred to as "fading rate constants". Characteristic fading curves were obtained by making graphs of fading rate constant against initial ΔE, i.e. before fading.

4. Results

Comparison of the different freshly dyed textiles, showed that some seemed to be of a different hue in addition to differing in their depth of dyeing. In particular it was noticed that the samples freshly dyed onto nylon were initially blue until after several minutes had passed when the hue settled to violet. The DBI on wool appeared redder than the samples on silk, cotton and linen but the samples on the nylons were bluest. The reflectance spectra of the dyed textiles were measured using the integrating sphere attachment of a Perkin-Elmer 551S ultraviolet/visible spectrophotometer and the wavelength absorption maximum, λ_{max} determined. The results of this examination are shown in Table 1 where comparable experimental results for similar indigo-dyed textiles are also shown for interest.

First order fading kinetics for the four DBI-dyed textiles are shown in Fig. 2.

Figs. 3 and 4 show characteristic fading curves for DBI on the textiles. To avoid too much data on one graph, the results for natural fibres and for the nylons are presented on separate graphs. In contrast with the data for the first order plots there

Table 1
Wavelength absorption maxima for reflectance spectra of textiles dyed with indigo and DBI

Textile substrate	λ_{max} Indigo (nm)	λ_{max} DBI (nm)
Cotton	662	538
Linen	662	532
Silk	628	528
Wool	660	522
Nylon 6	616	540, 594
Nylon 66	616	546, 593

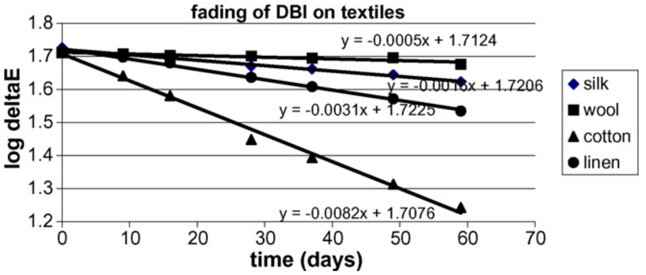

Fig. 2. The fading of four DBI-dyed textiles with different fibre types. These results illustrate the different rates of fading which can occur on textiles starting with approximately the same depth of dyeing.

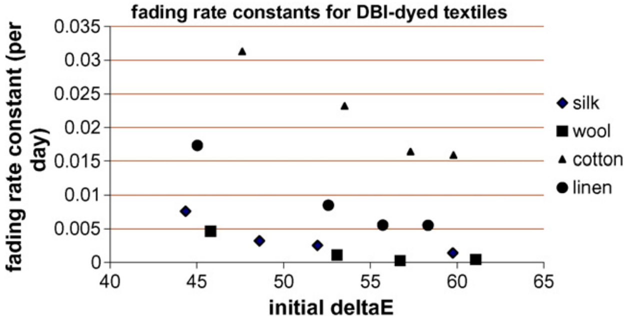

Fig. 3. The characteristic fading data for four natural materials dyed with DBI.

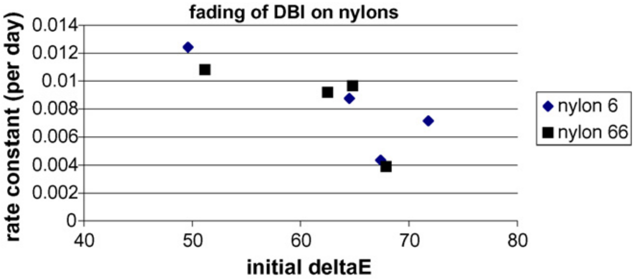

Fig. 4. The characteristic fading data for two types of nylon dyed with DBI.

is no a priori reason why any particular type of line should be drawn through the points and none has.

To enable comparisons of the fading kinetics for the rate of fading of indigo-dyed textiles with those of blue wool standards the fading rate constants were obtained for blue wool standards 2 to 6 using the same fading conditions as for the DBI dyed textiles. The results are shown in Table 2.

Table 2
Experimental fading rate constants for blue wool standards for comparison with the rate constants for fading DBI-dyed textiles

Blue wool standard number	Fading rate constant (per day)
2	0.028
3	0.0159
4	0.0046
5	0.0025
6	0.0012

5. Discussion

Samples of DBI dyed onto different fibre substrates showed that a wide range of hues were obtainable (as also shown by Cooksey and Sinclair [15]). It was found that DBI-dyed textiles faded at a significant rate in the light-fastness tester, however the rates varied with fibre type. Comparing fading over a range of initial depths of shade the rate of fading for dyed cotton was greatest, with linen the next greatest with wool and silk being slowest to fade. In terms of blue wool standard comparisons, pale dyeings of DBI on cotton had fastness less than BW 2 deeper shades were about BW 3. Linen gave pale dyeings of light-fastness BW 3 while deeper shades were BW 4. The characteristic curves for wool and silk overlapped but the silk dyeings obtained were not as dark as those on wool and thus generally faded faster with the palest at BW 4 then increasing to 6 with increasing depth while wool ranged from BW 4–5 up to 7 or 8.

For the both nylon samples the fading rates were similar but the rates of fading generally decreased with increasing depth of shade; comparable blue wool values ranged from 3 to 4.

According to the hypothesis proposed by Giles [21] the first order nature of the fading seen on all textiles demonstrates that the DBI molecules exist in a well dispersed state. Certainly, no individual particles of dye could be seen under 500× magnification on a transmitted light microscope. Giles suggests that this type of fading indicates that fading agencies are able to gain free access to the dye. The results obtained here clearly show that the fading rate constant for fading of DBI is higher for textiles containing least dye. This type of behaviour was also seen in indigo-dyed textiles in previous work [9].

Giles determined the change in light-fastness with dye concentration for azo dyes and produced a curve which he called the "characteristic fading curves". It was thought that the higher the concentration of dye, the larger was the size of the dye aggregates in the fibre. If it is assumed that the fading occurs at the surface of dye aggregates, it follows that the rate of fading will depend on the concentration of dye, with the smallest aggregates (low dye concentration) fading fastest.

It can be seen that for most depths of shade the fading rate constants for DBI on cellulosic fibres are higher than for proteinaceous fibres. However at initial ΔEs (compared to undyed textile) above about 65, the rate constants are much lower and suggests that the fugitive nature of the dye may be for all practical purposes negligible on many museum specimens.

Nylon was, of course, not available in the ancient world, however, it was hoped that the inclusion of the nylon samples might provide useful clues to the reasons behind the different fading rates found on different fibre types. The nylon samples had light-fastness corresponding to BW 3–4. The blueness of these samples might lead one to suspect the fugitive nature was linked to low degree of aggregation of the dye to which Cooksey and Sinclair alluded. However, the most light sensitive samples were dyed cotton, the purple hue of which might suggest a high degree of aggregation. The cause of the differences in light-fastness needs further consideration.

Textiles of this kind, in museums, are usually displayed in light-controlled environments where the illuminance is less than 50 lx with less then 75 μW/lm of ultraviolet light. In the author's experience the textile substrate for still existing, ancient DBI-dyed textiles is wool and the depth of shade is very high, thus the rate of fading will be sufficiently low for continuous display to be acceptable in most circumstances.

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