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Does argon anoxia cause a color change in Prussian blue pigment?

Daniel Koestler, Mary W. Ballard , A. Elena Charola  and Robert J. Koestler 

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ABSTRACT

The study focused on the effect of anoxic treatment on the discoloration of Prussian blue-dyed textiles and paper. Prussian blue pigment has been known to change color in the presence of light and heat in a vacuum for quite some time, but some claims were made that a low-oxygen environment alone contributed to its fading. The aim of this study was to determine whether argon anoxic treatment would induce the same changes when kept in the dark or in the light. The results clearly show that fading of Prussian blue in an argon anoxic condition occurs in the light but not in the dark.

RÉSUMÉ

Cette étude porte sur l'effet d'un traitement par anoxie sur la décoloration des textiles et des papiers teints au bleu de Prusse. Il est connu, depuis assez longtemps, que le bleu de Prusse change de couleur en présence de la lumière et de la chaleur lorsqu'il est sous vide. Mais on a aussi rapporté qu'un environnement privé d'oxygène pouvait à lui seul faire pâlir la couleur. Le but de cette étude visait à déterminer si un traitement par anoxie à l'argon induirait les mêmes changements de couleur lorsque le bleu de Prusse est conservé dans l'obscurité ou à la lumière. Les résultats montrent clairement que dans des conditions d'anoxie à l'argon le pâlisement du bleu de Prusse se produit à la lumière, mais non dans l'obscurité. Traduit par Elisabeth Forest.

RESUMO

O estudo teve por foco o efeito do tratamento com gás na descoloração de tecido têxtil e papel tingidos por azul da prússia. O azul da prússia é conhecido por mudar de cor no vácuo, na presença da luz e do calor, por um tempo prolongado, mas algumas reclamações foram feitas que um ambiente com baixo oxigênio, apenas, contribuiu para o seu desbotamento. O objetivo deste estudo foi determinar se o tratamento com anóxia de argônio induziria às mesmas alterações quando no escuro ou na luz. Os resultados claramente mostram que o desbotamento do azul da prússia, em condições de anóxia de argônio, ocorre na luz, mas não no escuro. Traduzido por Valeria Gauz.

RESUMEN

El estudio realizado se centró sobre la decoloración de textiles y papel teñidos con azul de Prusia durante tratamientos con anoxia. Es sabido que el pigmento azul de Prusia cambia de color en presencia de luz y calor en el vacío, sin embargo hubo un planteamiento sugiriendo que un ambiente con bajo contenido de oxígeno contribuye a su decoloración. El objetivo de este estudio fue determinar si un tratamiento anóxico con argón podía inducir los mismos cambios tanto si se realizaba en la oscuridad o en presencia de luz. Los resultados muestran claramente que la decoloración del azul de Prusia durante tratamientos anóxicos con argón sólo ocurre en la presencia de luz, no si se realiza en la oscuridad. Traducido por A. Elena Charola.

KEYWORDS

Argon; anoxia; Prussian blue; fading; light; substrate influence

1. Introduction

The use of argon gas to create low-oxygen environments has become an established treatment for the suffocation of fungi and insects in cultural property for many materials and objects (Koestler 1992, 2001; Koestler, Tavzes, and Pohleven 2004). As an inert gas, argon does not directly react with the materials in objects and its proper use poses no threat to human health. Thus, anoxia with argon is relatively safe for both treated

materials and humans; it is therefore favored for museum use, which often sees delicate objects requiring exposure to prolonged low-oxygen environments used in fumigation. Nitrogen is a similar and still-common suffocant, although it is not as effective or efficient as argon for anoxic treatment of infected objects (Valentin, Alguero, and Martin de Huas 1992). Most notably, argon has the advantage of being heavier than nitrogen and oxygen, thus displacing any oxygen that would otherwise

collect at the bottom of the treatment container; furthermore, argon has additional benefits over nitrogen for treatment of fungal infestations (Koestler, Tavzes, and Pohleven 2004).

Prussian blue pigment has been used extensively on many objects (Berrie 1997) and has been known to change color in the presence of light and heat in a vacuum (Chevreul 1837, 108–149; Nassau 2001, 143–152; Kirby and Saunders 2004, Ware 2008). Prussian blue has also been reported to change color on textiles in low-oxygen environments (Rowe 2004, used scavengers to create this environment; del Hoyo-Meléndez and Mecklenburg 2011; Beltran, Druzik, and Maekawa 2012). Rowe's work showed that Prussian blue on silk in a dark, high-nitrogen low-oxygen environment might have minimally changed, but in a well-lit, high-nitrogen low-oxygen environment the change was significant (although the actual level of oxygen was not measured). As a result of this study, Rowe recommended that textiles containing Prussian blue should not be treated or stored in an anoxic environment.

There are three unknowns with the Rowe (2004) study that may raise questions about the validity of the conclusion. First, no light control was reported (i.e., control kept in the dark); this would have demonstrated to what degree light exposure manifested the observed color change. Rowe implies that light exposure during anoxia had a much greater effect than simply anoxic conditions alone (please see Table 1 in paper 2004:265).

A second unaccounted factor in the Rowe study is the effect of surface texture (roughness) or fiber/yarn/weave orientation on the ΔE^* calculations. Surface roughness dramatically alters the ΔE^* value due to scattering of reflected light from the surface, as does the fiber/yarn/weave orientation. On a smooth surface a $\Delta E^* = 1.0$ may represent a real difference in color (Buss Brott and Cox Crews 2000), but on a rough surface it does not; even a ΔE^* of 4.0 (Tiano, Bracci, and Rescic 2003) may not represent a perceptible change on an irregularly textured surface, since the greater the surface roughness the greater the error in ΔE^* values measured by the instrument. For example, García and Malaga (2012) propose that a ΔE^* of 10 is still

acceptable in the case of stone surfaces. Other factors such as color tones play an important role (Brischke, Borcharding, and Mengel 2015), and overall, the consensus is that values of $\Delta E^* > 3$ are visually detectable (Boutin and Leroux 2000). In Table 1, (Rowe 2004), only two values stand out as unquestionably significant and both represent anoxic conditions with light – the first is Prussian blue, and the other is Prussian blue with tin. Since there are no control conditions for light vs. dark in either case, it is unclear how much of the change is due to anoxia and how much is due to light.

The third unknown is the actual oxygen level in the bag. Rowe (2004) used oxygen scavengers to remove the oxygen rather than nitrogen gas flow. Scavenger sachets have a definite shelf life; they have a low leakage rate that over time causes the scavenger to become saturated thus reducing their efficiency in removing oxygen once they are employed in an anoxia process. Without measuring the oxygen level during treatment, one cannot be sure of the actual effectiveness of the scavengers nor the actual oxygen level reached. Older scavengers absorb less oxygen more slowly than newly made scavengers. It should also be noted that the scavenger absorption process is exothermic – the higher the initial level of oxygen the hotter the scavenger gets. Scavengers placed too close to an object, e.g., a Prussian blue sample, may heat the sample up, contributing to fading, i.e., the thermochromic effect (Schroeder, Tsapatsaris, and Eastaugh 2008).

Earlier studies on different substrates did not find any change in Prussian blue under dark low-oxygen environments; one on oil-based paints (Koestler et al. 1993) and the other on acrylic paints (Suzuki and Koestler 2003). These earlier studies, also like Rowe's, did not adequately address any contribution from light.

2. Materials and methods

Samples of paper and silk were dyed with Prussian blue. For paper, Whatman filter paper No. 1 discs were used and dipped in a water-color (w/c) solution of Prussian blue prepared for this purpose (see Appendix 1 for details). Whatman No. 1 filter paper was also used to prepare the cyanotype (Ware 1999, 2014) samples (see Appendix 1 for preparation details) by cutting out 2 × 2 inch squares. A commercially available silk textile was dyed in-house as described in Appendix 2.

In addition, two wool standard reference fabrics were used from the International Organization for Standardization (ISO), No. 7 and 8; Standard 7 is vat dyed with solubilized Vat Blue 006 while Standard 8 used the solubilized Vat Blue 008. Vat dyes are produced by reduction

Table 1. List of samples used in the experiment.

Sample No.	Description
15	Prussian blue w/c on Whatman's No. 1 Paper
17,18	Prussian blue-dyed Silk
19,20	Cyanotype
21,22	ISO Blue Wool Standard No. 7
23,24	ISO Blue Wool Standard No. 8

and re-oxidation of the dyestuff (solubilized vats are rendered water-soluble in their leuco state; once in the fiber, the original vat dye is regenerated with a strong oxidizing agent, nitrous acid); a change under dark anoxic conditions would indicate an alteration of the standard itself. The inclusion of these standards was to confirm that they were not susceptible to the fading under the conditions of our experiment.

Duplicates for each sample type were prepared as listed in Table 1, with the exception of Whatman No. 1 paper dyed with Prussian blue, where only one sample proved to be correctly prepared. Excepting the wool standards, each sample was prepared individually and in-house, which explains the color variability within each sample and between the two specimens of each material.

Four specimens were prepared for each sample: two controls, one to be kept in the dark and the other exposed to light, and two anoxia-treated specimens to be subjected to either dark or light conditions. The exposure times were of four weeks, in each instance, as this is the typical length of an anoxic treatment for museum objects.

As a specific example, two of the dyed specimens were marked with a grid (Figure 1), using small dots of Winsor & Newton Titanium White or Golden Experimental Fluorescent Cerise paints; the location of these dots was suitably far removed from each sample area that the instrument could theoretically be out of alignment by as much as half a sample diameter without a dot being located under the instrument's measurement window. In practice, the dots ensured that such a misalignment never happened.

The two dyed specimens were then measured and subsequently cut into two smaller sample sections: one half for dark exposure and the other for light exposure

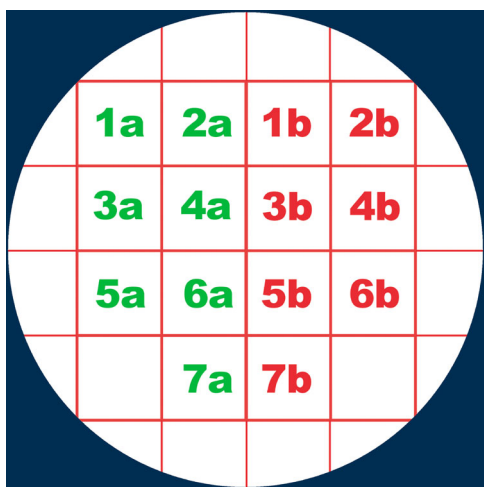


Figure 1. Alignment grid example, where green (a) on left, corresponds to the control and red (b) on right, to the sample subjected to anoxia.



Figure 2. Two samples of No. 18 Prussian blue-dyed silk are shown—marked and cut into two control specimens, before (B) and after (A) light (L) exposure. The diagonal arrows indicate the rough orientation used when aligning the spectrophotometer with the marked dots.

(Figure 2), so that they would correspond to the same original material and be as uniform in texture and appearance as possible. The same procedure applies to all the sample types in Table 1.

The two types of marking paint were chosen because they do not bleed onto the spots used for measurement – the purpose of the dots was to align the instrument precisely, to allow for a consistent relative orientation, angle, and positioning. That is, the red dots matched the translucent crosshairs outside the measurement area of the spectrophotometer. By pointing the spectrophotometer diagonally over the red dots (see Figure 2), the exact location could be measured and re-measured with accuracy. This alignment grid method provided six to eight different measurement spots on each half sample ($n = 6$ or $n = 8$). To minimize direct handling, each sample was adhered to a transparent Mylar film, which was cleaned with deionized water and attached to the back of each sample via a thin film of 3 M Spray Mount Artist's Adhesive. Preliminary tests had shown that this adhesive had no measurable effects on the results.

A HunterLab MiniScan® XE Plus spectrophotometer was used to read each measurement spot before each sample was sealed into a treatment or control bag. The instrument has a D6500 illuminant and a 10° standard observer, with a diffuse/8° (Sphere) optical geometry. An 8 mm diameter measurement area provided the L^* , a^* , and b^* values for each spot, in accordance with

the International Commission on Illumination (CIE) 1976 scale. The instrument was internally calibrated at the beginning of each series of measurements. The crosshairs of the sample window of the instrument corresponded to the dot grid on each sample as previously described, allowing for the measured spot to be read with consistency. Five consecutive readings were averaged per spot – the instrument was not repositioned between these measurements to help average away any variability created by the instrument itself. After treatment, both halves of each sample were juxtaposed again to allow for visual comparison between the control and treated sample and then photographed (Figure 2).

The other set of two specimens (per sample) were each placed in its own treatment bag; one was flushed with argon (industrial grade, < 20 ppm O₂) containing 55% relative humidity until the level of oxygen was < 500 ppm. The oxygen level was measured using an Illinois Instruments 2550 oxygen meter. When the oxygen level was low enough, the bags were inflated slightly and heat-sealed. No Ageless® or other oxygen absorption agent was used. This is the same process used for anoxic fumigation of cultural objects (for details of the process see Koestler, Tavzes, and Pohleven 2004). The second sample, serving as a control, was sealed in a bag without any flush-through, and thus contained the ambient environment of the room: ~50%RH with ~21,000 ppm O₂. Both of these bags were then placed in a dark room. To study the effects of anoxic conditions in light, the above procedure was repeated for each sample type. The prepared treatment and control bags were then placed near an east-facing window for exposure to normal office daylight. All samples were left in their respective conditions for four weeks, a standard length of time for fungal or insect fumigation using argon-rich, anoxic environments (Koestler, Tavzes, and Pohleven 2004).

The samples were removed from their bags individually at the end of the four-week treatment period. Color measurements were performed on each sample, again using the grid to align the instrument so that readings were taken on the same spots as before. For Whatman paper, cyanotype and silk, eight readings were taken on each specimen, but only six readings were taken for the two wool samples since these were standard samples and therefore more uniform.

The color difference, ΔE^* , between the before and after conditions for each sample was calculated by means of the 1976 CIE-L*a*b* color space standard formula (Urland 1999; AATCC 2004a – equivalent to ISO 105-J01; AATCC 2004b) in order to be able to compare them directly with previous in-house studies.

The ΔE^* was calculated for each individual spot from differences of L*, a* and b* readings, e.g., before and after

dark or light exposure, and averaging them for each specimen. It was also calculated by averaging all the readings, i.e., L*, a*, and b*, and calculating the ΔE^* from these averages, and as expected, they are similar but not identical. We also tested out the CIE ΔE_{2000} equation and found that the results obtained followed the same pattern to those obtained with the ΔE_{1976} , indicating that the results obtained with the latter were valid (see Appendix 3).

It was important to consider that faded Prussian blue can exhibit phototropy, spontaneously regaining color once re-exposed to an oxidizing environment (Berrie 1997; Kirby and Saunders 2004). In order to avoid this reversal, a steady stream of argon was flushed through the partially opened treatment bag during measurement and immediately prior to photography to reduce the exposure to oxygen in the air; again, this follows the previously discussed treatment and measurement procedures for museum objects. To minimize the chances of phototropy during the measurement process, the length of time samples were taken out of the bags before undergoing measurement was kept to a minimum. By utilizing the orientation marks on the Mylar film, samples in all cases were examined in the same orientation both before and after treatment.

3. Results and discussion

Table 2 summarizes the ΔE^* calculated for each individual spot from differences of L*, a*, and b* readings, as previously described, and averaging them for each specimen, and the corresponding standard deviations, ranging from 0.05 to 1.

The ΔE^* confirmed the preliminary observations that both cyanotype and silk changed significantly in color when exposed to anoxic conditions under light. This was also the case for the Whatman paper (No. 15)

Table 2. Calculated ΔE^* for the before/after exposure to dark or light.

Sample	No.	Control	Treated	Control	Treated
		Dark		Light	
Whatman paper	15	1.47 (0.25)	1.43 (0.23)	0.71 (0.11)	3.80 (0.28)
	17	0.29 (0.12)	1.24 (0.12)	0.41 (0.32)	16.10 (0.36)
Silk	18	0.66 (0.96)	1.32 (0.60)	0.66 (0.12)	15.44 (0.47)
	19	0.36 (0.20)	2.71 (0.51)	3.27 (0.62)	21.25 (0.90)
Cyanotype	20	0.65 (0.48)	2.07 (0.12)	2.60 (0.12)	19.14 (0.61)
	21	0.61 (0.11)	0.64 (0.11)	2.31 (0.15)	1.70 (0.06)
Wool No. 7	22	0.65 (0.31)	0.83 (0.46)	2.50 (0.11)	1.68 (0.13)
	23	0.29 (0.16)	0.38 (0.19)	1.12 (0.13)	0.70 (0.17)
Wool No. 8	24	0.29 (0.16)	0.25 (0.07)	1.10 (0.13)	0.79 (0.05)

Note: Calculated ΔE^* for the before–after exposure to dark or light data for both control and anoxic treated samples. Standard deviation is shown in parentheses, note that they are significantly higher for the in-house prepared samples. Light gray highlighted cells indicate a visible change in ΔE^* (>3). Note that the cyanotype control samples show a minimal change when exposed to light, one of which, sample 19, is only slightly above $\Delta E^* = 3$.

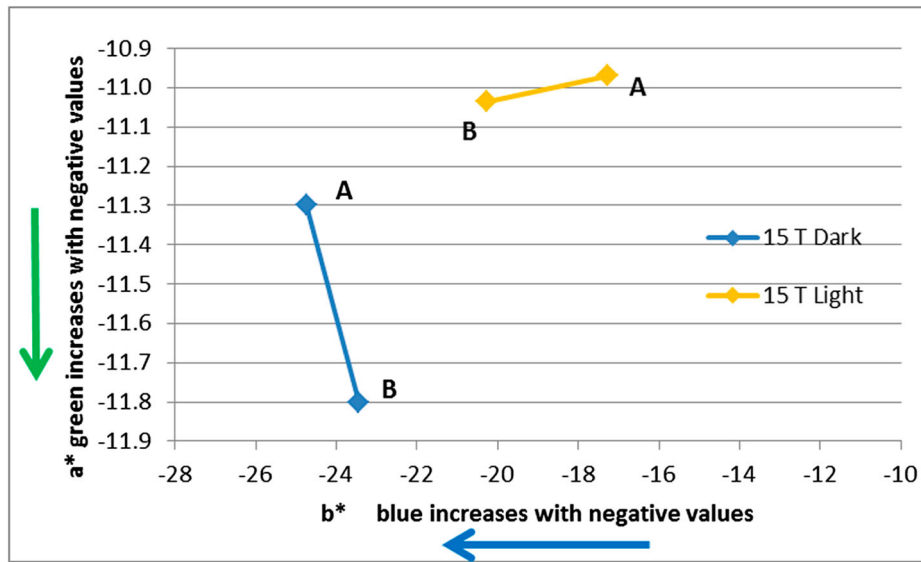


Figure 3. Changes of the a* and b* values for anoxic treated Whatman paper sample No. 15 before (B on graph) and after (A) exposure to dark or light conditions.

sample. No visible changes ($\Delta E^* > 3$) were observed for samples submitted to anoxic treatment when left in the dark. Only two samples showed high standard deviations (>0.90): the cyanotype treated in light (No. 19), and the silk control in dark (No. 18). Most of the control samples in light do not show fading, this could be attributed to the fact that the Prussian blue pigment has been shown to fade initially (first 10 h) and then slowly recover color (Korenberg 2008). The substrate will influence significantly this behavior. Neither standard wool textile (No. 7 and No. 8) showed any significant changes when subjected to dark or light, regardless of exposure to anoxic conditions. All wool samples had a standard deviation below 0.5, reflecting their color and surface uniformity.

The L^* , a^* , and b^* values, before and after exposure, for each sample are presented in Figures 3–8 (see Appendix 4 for all colorimetric data.) They reveal substantial information about the effect of anoxia exposure to the actual type of color change as well as its extent. The Whatman paper samples show changes for two axes, ΔL^* (dark–light) and Δb^* (yellow–blue), while the cyanotype shows significant changes for all three axes. On the other hand, silk shows only moderate changes limited to the ΔL^* and Δa^* (red–green) axes to samples exposed to argon anoxia. The following discussion examines how these individual measurements disclose the nature of the color changes in Prussian blue.

To focus this evaluation, the samples exposed in dark or light conditions in anoxic environment are compared,

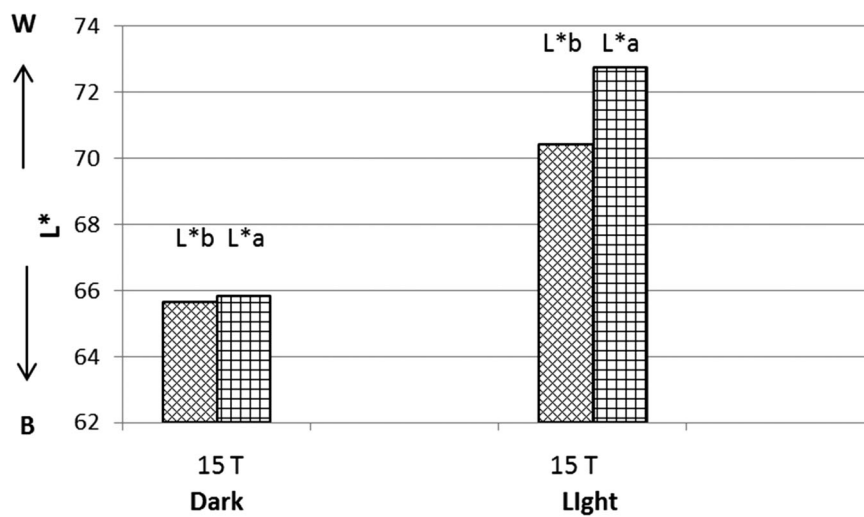


Figure 4. Change in L^* for the Whatman treated paper sample No. 15 before and after exposure to dark or light conditions. The intensity of the colors aims to show the difference between dark and light exposure.

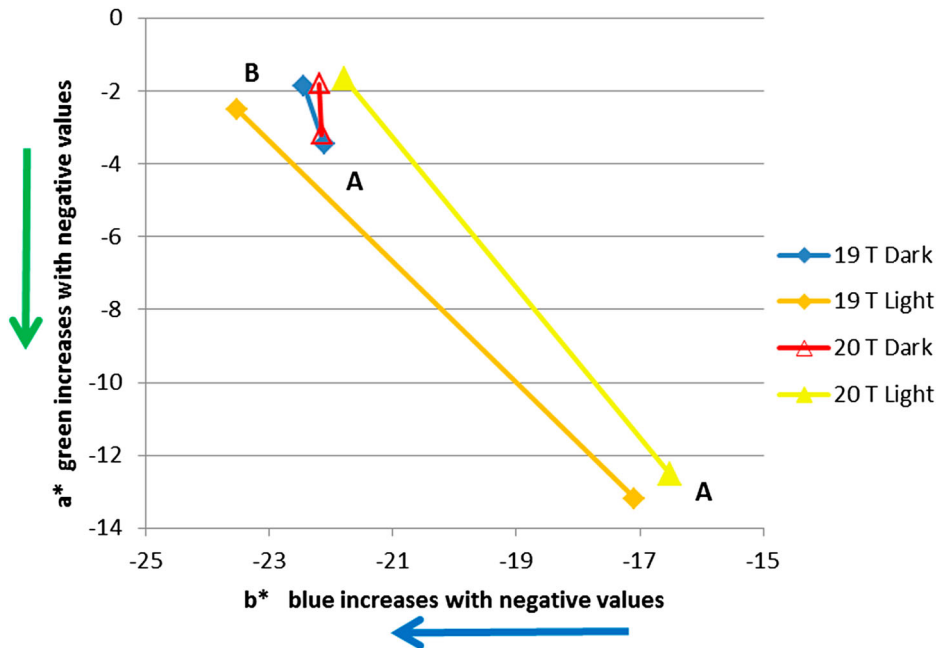


Figure 5. Changes of a^* and b^* values for anoxic treated cyanotype samples before (B) and after (A) exposure to dark or light conditions.

plotting the changes in a^* value as a function of the b^* ones for the Whatman paper No. 15 as shown in [Figure 3](#). Note that the relative scales used for the abscissa and the ordinate vary in the Cartesian graphs. The ΔL^* values, corresponding to the dark–light axis, are plotted as bar graphs in [Figure 4](#).

The graphs for the Whatman paper clearly show that treated samples in the dark had a minor increase in blue with a greater decrease in green while the L^* value remained nearly constant. On the other hand, when exposed to light, the treated samples show a large decrease in blue and a lesser one, practically negligible

for green, while the L^* value showed a significant increase indicating an overall lighter shade.

A similar analysis of the cyanotype data is provided below, where [Figure 5](#) shows the changes of a^* values as a function of b^* , while the L^* data is plotted in [Figure 6](#). The change in a^* and b^* values are small under anoxia in the dark, but there is a substantial change when the samples are exposed to anoxia while lit. A difference appears in the L^* value between dark anoxia and light exposed anoxia. Note the ordinate scale for the ΔL^* in [Figure 6](#) is much larger than for that in [Figure 4](#); light exposure during anoxia causes a profound effect on the cyanotype samples.

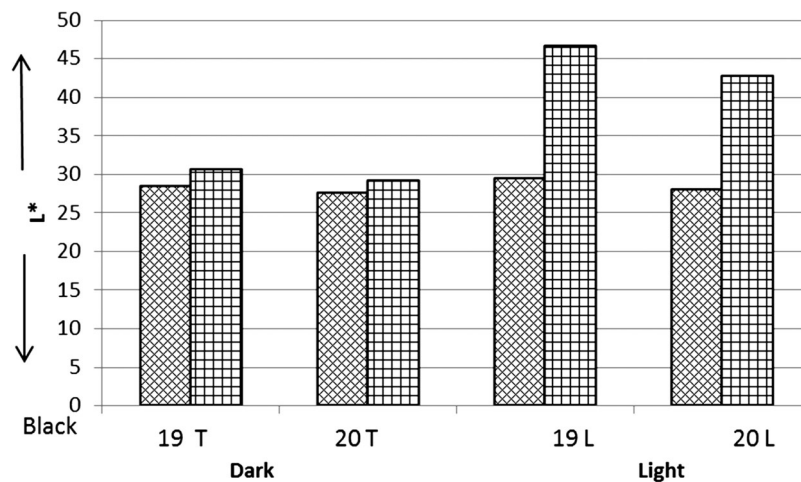


Figure 6. Change in L^* for cyanotype before and after exposure to dark or light conditions.

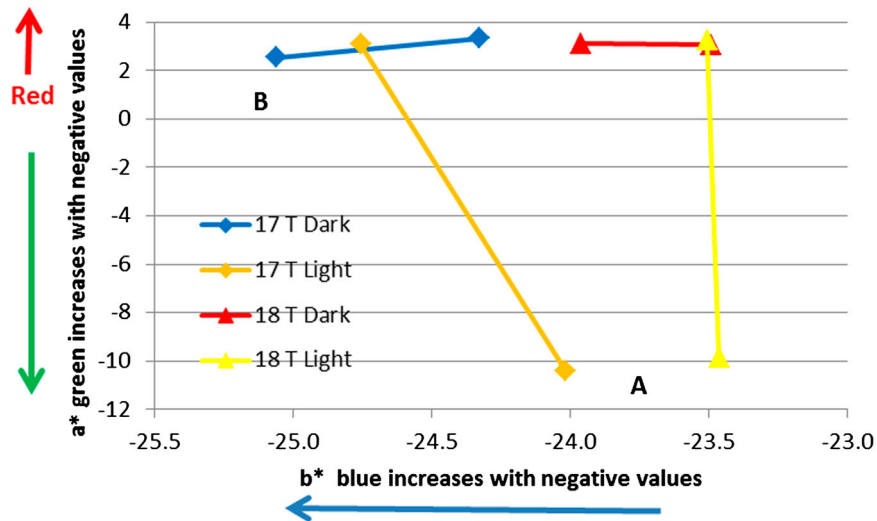


Figure 7. Changes of a* and b* values for anoxic treated Prussian blue dyed silk samples before (B) and after (A) exposure to dark or light conditions. Note that the silk samples in the dark have a* values in the red section of that axis, with a significant shift to the green section after light exposure.

Samples for both Whatman paper (No. 15) and cyanotype (No. 19, 20) show a decrease in the intensity of the blue when exposed to light under anoxic conditions. However, after comparing the data obtained for both samples it is evident that the difference for the Whatman No. 15 sample is far smaller and erratic than for the two cyanotype samples, even though the substrate is the same. However, the results obtained are valid and show that paper is a heterogeneous, porous composite, as defined by Ngo et al. (2011).

The corresponding plots for the silk samples are shown in Figures 7 and 8.

In the case of silk, it is evident that the samples under anoxic conditions kept in the dark show some slight, non-significant fading, with $\Delta L^* < 1$. However, when exposed to light, the fading is significant, with a change

in the a* axis from red to green and only a slight lightening of the blue color (b* axis), and a significant change of $\Delta L^* \sim 8.5$. This is in accordance with some of the results obtained in a previous study by del Hoyo-Meléndez and Mecklenburg (2011) which showed that in an anoxic environment there is a reduction in red (a* value). Similar results were also described by Rowe (2004) and by Chevreul in 1837, as reported by Padfield and Landi (1966).

It has long been known that lightfastness is not a property of the dye itself but of the dye-substrate complex, including other components used, such as mordants (Schwen and Schmidt 1959), and that color fading is not only due to changes along the dark-light axis, but also in hue and chroma, as found for the three samples tested.

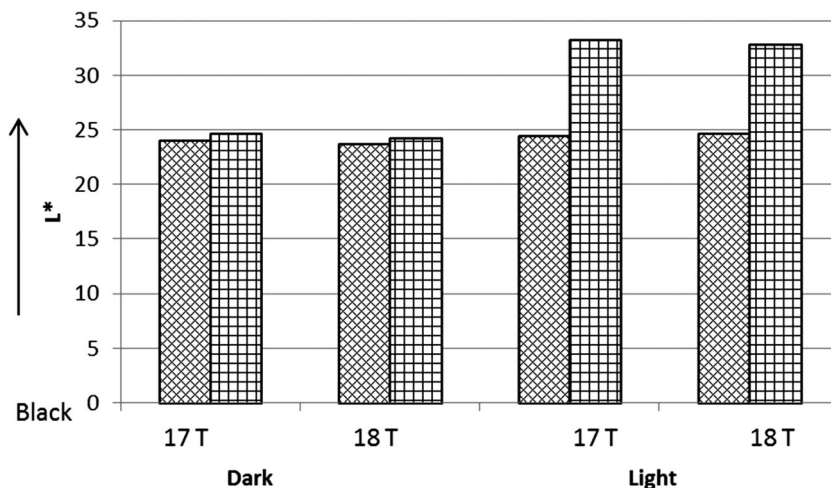


Figure 8. Change in L* for the anoxic treated silk samples before and after exposure to dark or light conditions.

Table 3. Results of the t -test for the ΔE^* Control–Treated samples.

Sample		C–T	C–T	t table	Degrees
		BD/BL	AD/AL	@ 95% CL	freedom
Whatman	15	1.30	4.63	2.14	14
	17	0.99	50.0	2.14	14
Silk	18	2.33	35.3	2.14	14
	19	0.43	23.3	2.14	14
Cyanotype	20	2.00	33.2	2.14	14
	21	1.84	0.68	2.23	10
Wool No. 7	22	0.34	2.90	2.23	10
	23	0.10	0.52	2.23	10
Wool No. 8	24	0.76	1.20	2.26	9

Note: Highlighted samples do not pass the t -test at 95% confidence level. Results of the t -test for the $\Delta E_{\text{Control–Treated}}$ before exposure to dark and to light (C–T BD/BL), as well as after exposure to dark and light (C–T AD/AL). Also listed are the critical t values at 95% confidence level for a two tailed distribution and the corresponding degrees of freedom.

Statistical analysis via the classical Student t -test was carried out to confirm the above assumptions based on the comparison of the $\Delta E_{\text{Control–Treated}}$ before exposure to dark and to light (C–T BD/BL), as well as after exposure to dark and light (C–T AD/AL). Table 3 presents the results showing that Whatman No. 15, silk, and cyanotype samples all show a significant difference between the control and the treated samples after dark exposure and after light exposure. Unexpectedly, one of the wool samples (No. 22) also showed a small difference, however, it would pass at a 99% confidence level (or a 0.01 probability, $t = 3.17$), while none of the others show a difference, even at a 99.9% confidence level (0.001 probability, $t = 4.14$).

4. Conclusions

This study showed that argon anoxic treatment itself does not affect the Prussian blue dye for the four-week duration (a typical treatment time) as long as it is kept in the dark. It examined the relative contributions of anoxia and light to potential color change in paper and silk samples for Prussian blue and cyanotype. In addition, two wool standards were also tested. In all cases, argon anoxia caused no statistically significant change in the dark. The vat dyed wool reference standards with high lightfastness did not turn into their leuco state in the absence of oxygen, nor fade. However, when the treatment is done in the light, there was a marked change in color for the Prussian blue paper and silk samples. The light treatment results with argon parallel Rowe (2004) results with nitrogen. Both anoxia treatments, in the light, caused Prussian blue pigments to fade. This raises some interesting questions about what the effect of light really is and whether it is the total flux or specific wavelengths causing the changes. Could the light be causing a thermal change in the colorants? This seems to be what happens in the Gervais et al. (2013a, 2013b) synchrotron studies. The thermal color shift seen in the synchrotron research may also explain the color

shift reported in a microfadometer study by del Hoyo-Meléndez and Mecklenburg (2011). In all cases, it is not the anoxic environment that causes the most color shift but the actinic energy imparted into the system by the measuring device (Konica Minolta 1998, 52).

The study has clearly shown that the fading of Prussian blue in an anoxic environment is caused by light, however, the effect of light on the chemical reactivity of the undyed substrate has not been studied as thoroughly. Some papers addressed this issue, for example, Gervais et al. (2014) studied in detail both cotton and linen substrates before and after dyeing. Silk has been studied for its light stability when attached to a substrate with an adhesive (Karsten and Kerr 2002). Other studies evaluated the influence of the substrate in the fading (del Hoyo-Meléndez and Mecklenburg 2011; Gervais et al. 2015). Further studies are needed to more fully address this issue and whether thermochromism is also at work with Prussian blue remains to be determined; but photochromism definitely occurs in light (Zollinger 1987; Berns 2000; ASTM 2001).

The practical conclusion of the current study is that argon anoxic treatment to control insects or fungi should be carried out in the dark, especially when Prussian blue may be part of the object. This is probably true for a nitrogen anoxic environment too. This is a refinement of the conclusions that Rowe (2004) gave wherein she recommended that no anoxic environment be used. Results from the current study suggest that her recommendation should be amended to include “when exposed to light.”

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Disclosure statement

No potential conflict of interest was reported by the authors.

Notes on contributors

Daniel Koestler is a visiting researcher at the Smithsonian’s Museum Conservation Institute and a software engineer for Adobe Systems. He has previously worked with the argon-anoxia treatment method for cultural property at MCI as an intern, and recently had the opportunity to return and finish an investigation of the effects of argon treatment on Prussian blue. His work at Adobe principally concerns architecting Big Data analytics solutions for Adobe’s digital marketing platform. Address: 4204 Dandridge Terrace, Alexandria, VA 22309. USA. E-mail: d.l.koestler@gmail.com

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References

- AATCC (American Association of Textile Chemists and Colorists). 2004a. Evaluation procedure 6: Instrumental color measurement. *AATCC Technical Manual* 79: 385–390.
- AATCC (American Association of Textile Chemists and Colorists). 2004b. Evaluation procedure 7: Instrumental assessment of the change in color of a test specimen. *AATCC Technical Manual* 79: 391–392.
- ASTM (American Society for Testing Materials). 2001. E-284-01 standard terminology of appearance. *Annual Books of ASTM Standard 2002: Section 6, Volume 06.01 Paint—Tests for Chemical, Physical, and Optical Properties: Appearance* 728–747.
- Beltran, V. L., J. Druzik, and S. Maekawa. 2012. Large-scale assessment of light-induced color change in air and anoxic environments. *Studies in Conservation* 57 (1): 42–57.
- Berns, R. 2000. *Billmeyer and Saltzman's Principles of Color Technology*. 3rd ed. New York: John Wiley & Sons.
- Berrie, B. H. 1997. Prussian blue. In *Artists' Pigments: A Handbook of their History and Characteristics (Vol. 3)*, edited by E. W. Fitzhugh, 191–217. Washington, DC: National Gallery of Art.
- Boutin, F., and L. Leroux. 2000. Color and weight evolution of limestones protected by water repellents after a three-year ageing period in urban environment. In *9th International Congress on Deterioration and Conservation of Stone (Vol. 2)*, edited by V. Fassina. Amsterdam: Elsevier.
- Brischke, C., T. Borcharding, and U. Mengel. 2015. Subjective sensation of color differences – Determination of thresholds depending on color tones and resolution. *Restoration of Buildings and Monuments* 21 (1): 21–27.
- Buss Brott, J. J., and P. Cox Crews. 2000. Influence of nitrogen gas and oxygen scavengers on fading and color change in dyed textiles. In *Textile Specialty Group Postprints*, edited by J. L. Merritt and V. J. Whelan, 55–67. Washington, DC: American Institute for Conservation.
- Chevreul, M. E. 1837. *Recherches sur la Teinture. 3e Série Recherches chimiques. "Sixième Mémoire,"* Paris, Imprimerie L. Martinet 1847, pp. 108–149. <https://books.google.com/books?id=KRYzAQAAAMAJ&pg=RA2-PA1&lpg=RA2-PA1&dq=REcherches+chimiques+sur+la+teinture&source=bl&ots=S79GtGWZqr&sig=6f8EJNgp8fb3tneKTYyQmSeWxZw&hl=en&sa=X&ved=0ahUKEwJS-un8h6vbAhXjtlkKHWT-A24Q6AEINjAD#v=onepage&q=REcherches%20chimiques%20sur%20la%20teinture&f=false>.
- del Hoyo-Meléndez, J. M., and M. Mecklenburg. 2011. The use of micro-fading spectrometry to evaluate the light fastness of materials in oxygen-free environments. *Spectroscopy Letters* 44: 113–121.
- García, O., and K. Malaga. 2012. Definition of the procedure to determine the suitability and durability of an anti-graffiti product for application on cultural heritage porous materials. *Journal of Cultural Heritage* 13 (1): 77–82.
- Gervais, C., M.-A. Languille, G. Moretti, and S. Réguer. 2015. X-ray Photochemistry of Prussian blue cellulosic materials: Evidence for a substrate-mediated redox process. *Langmuir* 31 (29): 8168–8175. doi:10.1021/acs.langmuir.5b0070.
- Gervais, C., M.-A. Languille, S. Reguer, C. Garnier, and M. Gillet. 2014. Light and anoxia fading of Prussian blue dyed textiles. *Heritage Science* 2: 26. doi:10.1186/s40494-014-0026-x.
- Gervais, C., M.-A. Languille, S. Reguer, D. Gillet, E. P. Vicenzi, S. Chagnot, F. Baudelet, and L. Bertrand. 2013a. 'Live' Prussian blue fading by time-resolved X-ray absorption spectroscopy. *Applied Physics A* 111: 14–22. doi:10.1007/s00339-013-7581-y.
- Gervais, C., M.-A. Languille, S. Reguer, D. Gillet, E. P. Vicenzi, S. Chagnot, F. Baudelet, and L. Bertrand. 2013b. Why does Prussian blue fade? Understanding the role of the substrate. *Journal of Analytical Atomic Spectrometry* 28: 1600–1609. doi:10.1039/C3JA50025J.
- Karsten, I. F., and N. Kerr. 2002. The properties and light stability of silk adhered to sheer silk and polyester support fabrics with poly(vinyl acetate) copolymer adhesives. *Studies in Conservation* 47 (3): 195–210.
- Kirby, J., and D. Saunders. 2004. Fading and colour change of Prussian blue: Methods of manufacture and the influence of extenders. *The National Gallery Technical Bulletin* 25 (1): 73–99.
- Koestler, R. J. 1992. Practical application of nitrogen and argon fumigation procedures for insect control in museum objects. In *Preprints of the 2nd International Conference on Biodeterioration of Cultural Property*, edited by K. Toishi, H. Arai, T. Kenjo, and K. Yamano, 94–96. Tokyo:

- International Communication Specialists. Yokohama, Japan; ISBN 9784990027919.
- Koestler, R. J. 2001. Detecting and controlling insect infestation in fine art. In *Pacific 2000, Proc. 5th International Conference on Easter Island and the Pacific*, edited by C. M. Stevenson, G. Lee, and F. J. Morin, 541–545. Los Osos, CA: Easter Island Foundation.
- Koestler, R. J., E. Parreira, E. D. Santoro, and P. Noble. 1993. Visual effects of selected biocides on easel painting materials. *Studies in Conservation* 38: 265–273.
- Koestler, R. J., Č Tavzes, and F. Pohleven. 2004. A new approach on conservation of wooden heritage. In *The International Research Group on Wood Preservation. Section 4. Processes and Properties*. IRG35, Ljubljana, Slovenia. Stockholm, Sweden: IRGWP. <http://www.irg-wp.com/irgdocs/details.php?0b064959-0b8b-47de-a007-a179898eecd/>.
- Konica Minolta Sensing, Inc. 1998. *Precise Color Communication: Color Control from Perception to Instrumentation. The Essentials of Imaging*. Osaka: Konica Minolta Sensing, Inc.
- Korenberg, C. 2008. The photo-ageing behaviour of selected watercolour paints under anoxic conditions. *The British Museum Technical Research Bulletin* 2: 49–57.
- Nassau, K. 2001. *The Physics and Chemistry of Color: The Fifteen Causes of Color*. 2nd ed. Somerset: John Wiley & Sons.
- Ngo, Y. H., D. Li, G. P. Simon, and G. Garnier. 2011. Paper surfaces functionalized by nanoparticles. *Advances in Colloid and Interface Science* 163: 23–38.
- Padfield, T., and S. Landi. 1966. The light-fastness of the natural dyes. *Studies in Conservation* 11 (4): 181–196.
- Rowe, S. 2004. The effect of insect fumigation by anoxia on textiles dyed with Prussian blue. *Studies in Conservation* 49: 259–270.
- Schroeder, S. L. M., N. Tsapatsaris, and N. Eastaugh. 2008. High-throughput and in Situ X-ray absorption spectroscopy of pigment libraries. In: *CHRESP: 8th EC Conference on Sustaining Europe's Cultural Heritage*, Ljubljana, Slovenia, 50–51. https://www.si.edu/mci/downloads/CHRESP%202008/CHRESP_proof_2008_LJUBLJANA.pdf.
- Schwen, G., and G. Schmidt. 1959. Some experiments on the effect of dye, fibre, and atmosphere on light fastness. *Journal of the Society of Dyers and Colourists* 75: 101–105.
- Suzuki, J., and R. J. Koestler. 2003. Visual assessment of biocide effects on Japanese paint materials. In *Art, Biology, and Conservation: Biodeterioration of Works of Art*, edited by R. J. Koestler, V. R. Koestler, A. E. Charola, and F. E. Nieto-Fernandez, 410–425. The Metropolitan Museum of Art, New York. New Haven: Yale University Press.
- Tiano, P., S. Bracci, and S. Rescic. 2003. Biomediated calcite precipitation for the reinforcement of monumental stones. In *Art, Biology, and Conservation: Biodeterioration of Works of Art*, edited by R. J. Koestler, V. R. Koestler, A. E. Charola, and F. E. Nieto-Fernandez, 486–497. The Metropolitan Museum of Art, New York. New Haven: Yale University Press.
- Urland, A. 1999. *Colour. ARC Laboratory Handbook* 5. Rome: ICCROM-UNESCO-WHC.
- Valentin, N., M. Alguero, and C. Martin de Huas. 1992. Evaluation of disinfection techniques for the conservation of polychrome sculpture in Iberian museums. In *Conservation of the Iberian and Latin American Cultural Heritage*, edited by H. W. M. Hodges, J. S. Mills, and P. Smith, 165–167. London: International Institute for Conservation of Historic and Artistic Works.
- Ware, M. 1999. *Cyanotype: The History, Science and art of Photographic Printing in Prussian Blue*. London: Science Museum.
- Ware, M. 2008. Prussian blue: Artists' pigment and chemists' sponge. *Journal of Chemical Education* 85 (5): 612–621.
- Ware, M. 2014. *Cyanomicon*. <http://unblinkingeye.com/Cyanomicon.pdf>.
- Zollinger, H. 1987. *Color Chemistry: Syntheses, Properties and Applications of Organic Dyes and Pigments*. New York: VHC.

SOURCES OF MATERIALS

Golden experimental fluorescent cerise (no longer available)
Golden Artist Colors, Inc.
188 Bell Road
New Berlin, NY 13411-9527
Telephone: 607-847-6154
USA

Winsor & Newton Professional Water Colour Titanium White (Opaque White)
TALAS
330 Morgan Avenue
Brooklyn, NY 11211
Telephone: 212-219-0770
www.talasonline.com/
USA

Appendices

Appendix 1. Procedures for manufacturing dyed whatman paper and cyanotype samples

(A) Manufacturing Prussian blue watercolor and dyeing Whatman paper

Materials

Kremer Pigments Prussian blue pigment
Kremer Pigments Gum Arabic
Deionized water
Whatman 5.5 cm filter paper
Paintbrush
Small plastic trays
Palette Knife

Preparation

- (1) Wash all tools and glassware with detergent and deionized H₂O.
- (2) Mix 4 mL of gum arabic with 12 mL of deionized H₂O to make a solution of gum Arabic and deionized water at a 1:3 ratio.
- (3) Add 0.6 g of Kremer Pigments Prussian blue pigment to the solution and stir.
- (4) Paint out one sample on Whatman filter paper using a brush. Apply three coats of watercolor, switching the direction of the brush strokes with each coat.

- (5) Further dilute the color with 8 mL of deionized H₂O for a thinner consistency.

Notes: Watercolor may be diluted with as much or as little water, depending on the desired consistency.

Notes from the Studio: Watercolor. Raw Materials for Fine Arts, Conservation, Woodfinishing, and Design. Kremer Pigments: New York, 2004.
Pigments and Materials for Restoration, Interior Design and Fine Arts. Kremer Pigments: San Francisco, 2007.

Dyeing

- (1) Wash all tools and glassware with detergent and deionized water.
- (2) Using tweezers, dip a piece of circular Whatman 5.5 cm filter paper into the Prussian blue watercolor.
- (3) Apply three coats, allowing excess paint to run off the paper in between each dipping.
- (4) Lay the coated paper onto a clean paper towel to remove excess paint and create an even coat. Use a new paper towel for each sample.
- (5) Flip each sample three times onto a clean area of the towel. After the second time, roll a glass stirring rod over each side of the paper to give it a flat, even coat. Use the glass stirring rod like a rolling pin. Clean it periodically in deionized water to avoid leaving excess paint on the sample.
- (6) Puncture the sample with a pin and attach it to cardboard to dry. Stand the cardboard in a vertical position so the samples do not come in contact with it.

(B) Manufacturing cyanotypes

Materials

Bostick & Sullivan (Santa Fe, NM) Cyanotype Kit: Solutions A & B; 2 eyedroppers; Instructions
3% hydrogen peroxide
Deionized water
Whatman No. 1 paper
2–6"x6" clear glass plates
2–13"x9" clear glass pans
Glass beakers
Paintbrush
Brown paper

Process

- (1) Wash all tools and glassware with detergent and deionized water.
- (2) Cut an 8"x8" piece of Whatman No. 1 paper, and lightly mark a 6"x6" square with a pencil.
- (3) Mix 42 drops of Solution A and 42 drops of Solution B together in a 100 mL glass beaker.
- (4) Dip a brush into deionized H₂O, and wipe excess H₂O off on a paper towel. This will help to prevent the solution from wicking up the bristles.
- (5) Pore the cyanotype solution in the center of the paper, and then brush it evenly around the 6"x6" square.

- (6) Place the cyanotype on a piece of thick brown paper, and then place it in a dark drawer to dry. Allow the paper to completely dry for about 1–2 hours.
- (7) Remove the paper from the drawer and place it between two glass plates. Expose the paper in direct sunlight, with the coated side face down. The emulsion will immediately begin to darken from a green color to a dark blue. The cyanotype must be overexposed until it begins to lighten to a gray color. Expose for approximately 10 minutes.
- (8) Wash the exposed paper in a cool water bath in a glass pan for 12 minutes. Change the water approximately every two minutes.
- (9) Make a developer of 100 mL 3% hydrogen peroxide and 900 mL deionized H₂O in a glass pan while the water bath was running. Wash the paper in the developer for 90 seconds. At this point the paper should turn a dark prussian blue color.
- (10) Place the cyanotype back in the water bath for another 8–10 minutes.
- (11) Lay the cyanotype on paper towels on the table and allow it to dry to a damp state. Then the paper can be hung on a makeshift clothesline to complete the drying process.

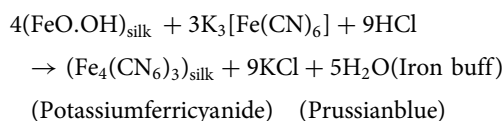
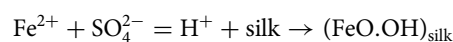
Results

The cyanotype was cut into nine 2"x2" squares. The value of the Prussian blue color depends on the length of exposure. Cyanotypes can also be exposed using a UV lamp. It was easier to use direct sunlight because the UV lamp requires a room where no light can get in.

The Whatman paper used was a light weight paper that absorbed the solution immediately upon contact. This made it difficult to spread the solution evenly and cover the entire square. The amount of solution the instructions called for had to be tripled to accommodate this problem.

Appendix 2. Dyeing silk samples to form Prussian blue

This procedure is called mineral dyeing because the inorganic components of the colorant are formed or synthesized *in situ* upon the fiber in a two-step process:



This recipe is based on silk in the gum. The silk is degummed, i.e., the sericin that covers the fibers is removed prior to treatment; the degumming liquor is reserved as an auxiliary in the mineral dyeing. After drying, the degummed silk is weighed on an analytical balance to ± 0.1 mg.

Mineral dyeing procedure:

There are two component parts to the creation of Prussian blue:

- (1) Following a preparatory acid rinse, the silk is then treated with an "Iron Liquor" and that treatment is fixed on the

fiber with the aid of the degumming solution (see details below).

- (2) A second solution is made combining solutions of potassium ferricyanide and of hydrochloric acid; once diluted and heated; the silk is immersed in the second solution to synthesize the blue color in the fiber (see details below).

After a thorough rinsing in deionized water the silk is allowed to dry.

Prussian blue is defined as an insoluble, fast dye composed of ferric ferrocyanide formed directly on the fiber. It can be discharged (returned to Iron Buff) by treatment with an alkali such as a mild soap.

A. Preparation of the iron liquor

(Note that the following procedure does not conform to modern laboratory safety procedures).

- Carefully combine 83 parts by weight of ferrous sulfate, 5 parts (by weight) concentrated sulfuric acid (18 M ~ 66° Baumé¹), and 13 parts (by weight) of concentrated nitric acid (16 M). This mixture will smoke and foam. After the mixture stabilizes, dilute with deionized water to a specific gravity of 33° Bé (1.29 specific gravity).

**** IMPORTANT: for safety reasons, a lower water volume is used into which the mixture is poured (rather than the reverse) and then taken to the correct final density by addition of more water.**

- Degummed silk is wetted in a dilute (5% v/v, about 4.7° Bé) solution of sulfuric acid.
- Remove the silk and immerse it in the iron liquor solution for 1 hour at room temperature.
- The silk is taken out and rinsed with deionized water.
- It is then immersed in the alkaline degumming bath and simmered at 90° C for 1 hour.

- It is taken out, rinsed with deionized water, and allowed to dry. The fabric is re-weighed.
- If a deep shade of blue is desired, this step is repeated.

The resulting “iron buff” is defined as a fast dye composed of hydrated ferric oxide formed on the fiber by the action of an alkali on an iron salt. It can be discharged (returning the fabric to its undyed state) by treatment with a dilute mineral acid.

B. Preparation of potassium ferricyanide solution:

- Based on the current dry weight of the fabric (owf), a mixture of 10% owf of potassium ferricyanide [$K_3Fe(CN)_6$] and 10% owf of concentrated hydrochloric acid (HCl 12 M) are mixed together. This mixture needs to be diluted with deionized water to create a “liquor ratio” (volume of the solution/weight of the silk) of 100:1.

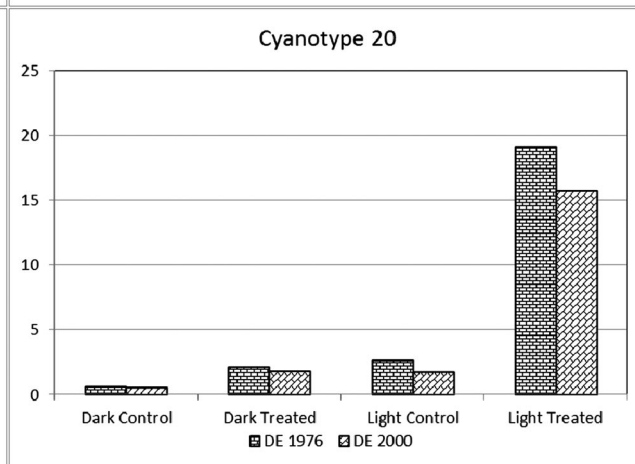
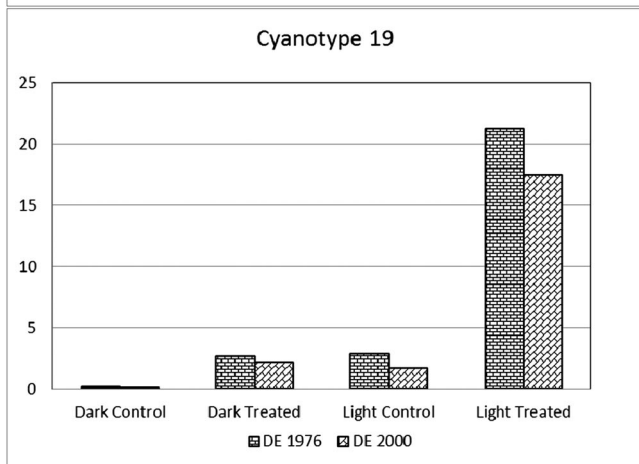
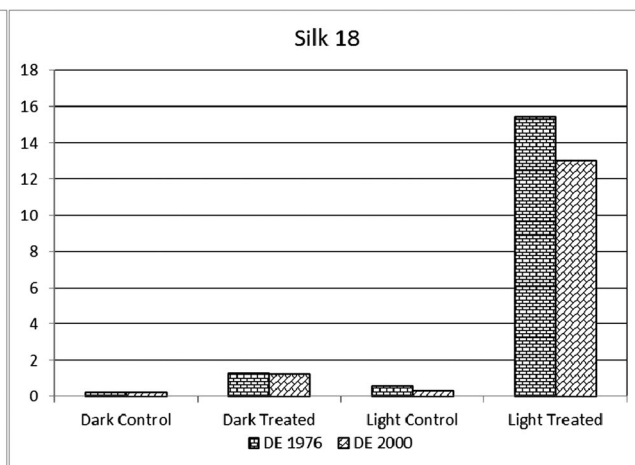
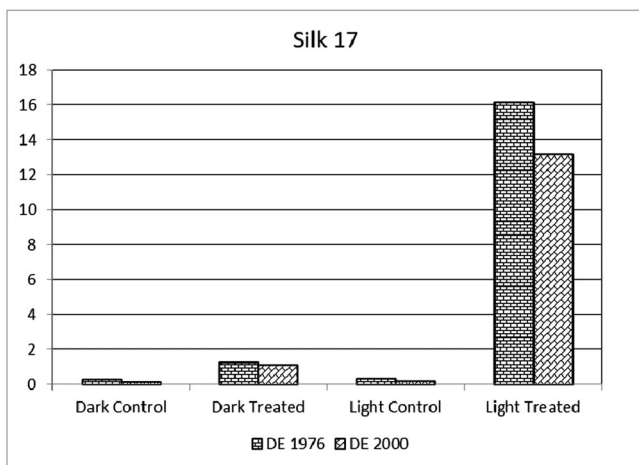
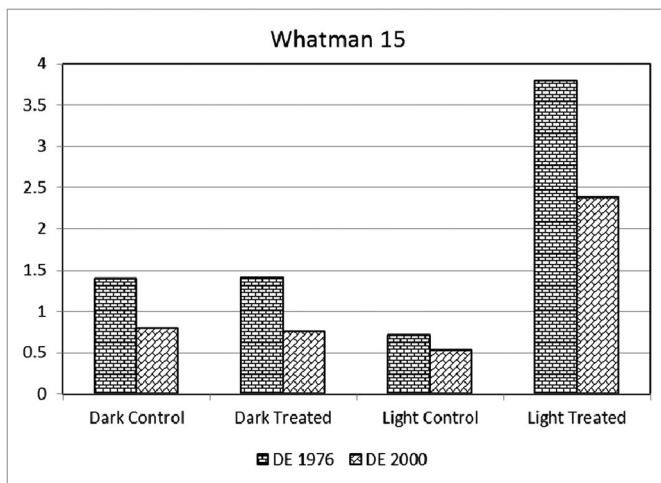
****IMPORTANT: for safety reasons, a lower water volume is used into which the mixture is poured (rather than the reverse) and then taken to the correct final volume by addition of more water.**

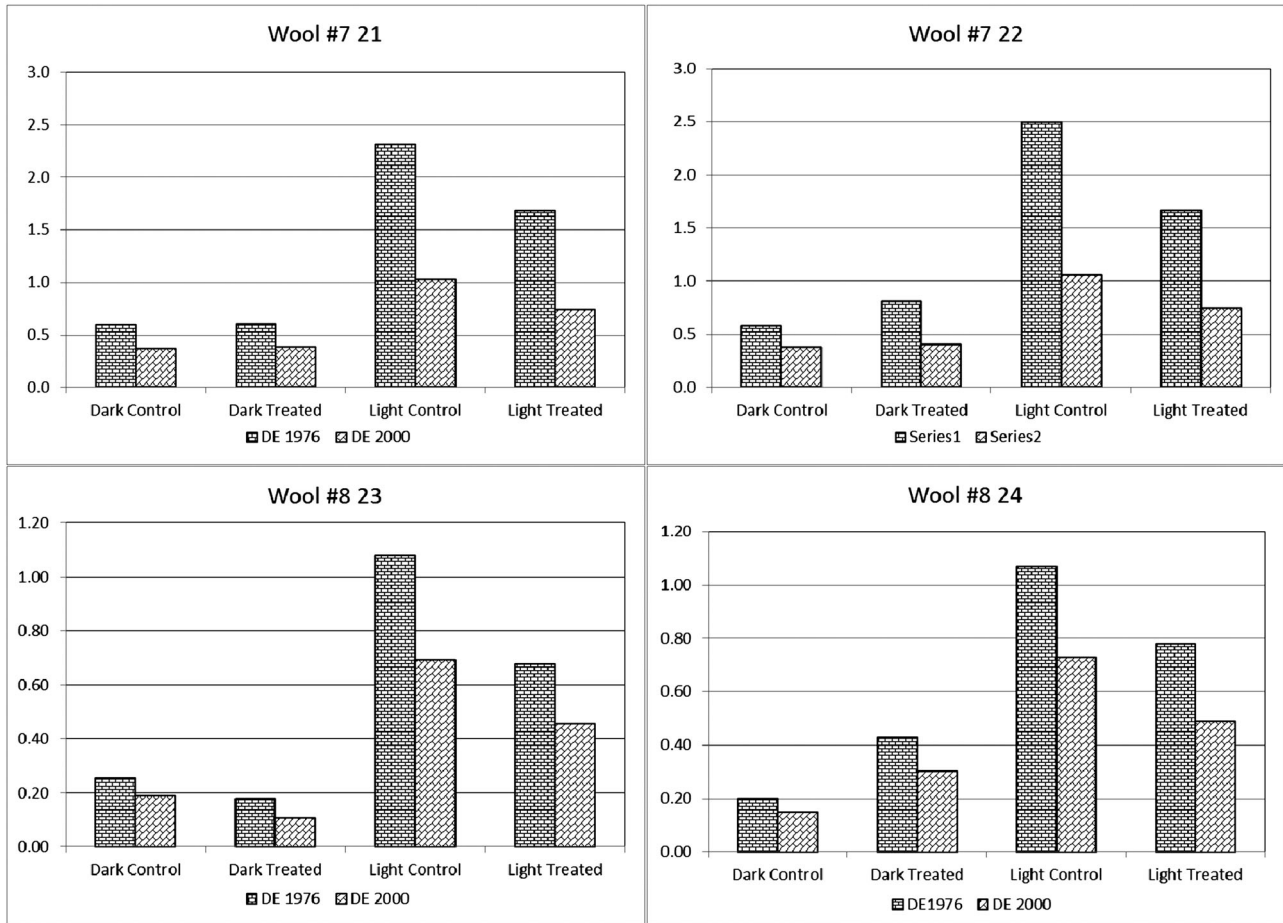
- The solution is heated to 50°C; the silk sample is then immersed into the heated solution for 1 hour and maintained at that temperature.
- The silk sample is taken out, rinsed thoroughly with deionized water and left to dry.

For further information please consult the following publications: Carboni, P. 1952. *Silk: Biology, Chemistry, Technology*, translated by K. Walter. London: Chapman & Hall, Ltd; Knecht, E., C. Rawson, and R. Loewenthal. 1910. *Manual of Dyeing*, 2nd edition. Vol 1. London: Charles Griffin and Company, Ltd.; and Trotman, E. R. 1975. *Dyeing and Chemical Technology of Textile Fibres*, 5th edition. High Wycombe, England: Charles Griffin and Company, Ltd.

¹Degrees Baumé (Bé) measure the density of a solution, using a Baumé hydrometer which is introduced into the solution and will partly submerge according to the solution's density.

Appendix 3. Comparison graphs CIE ΔE 1976 and CIE ΔE 2000 for all samples. Vertical axis corresponds to ΔE^*





Appendix 4. Averaged colorimetric readings

Sample		Control		Treated		Control		Treated	
		b-D	a-D	b-D	a-D	b-L	a-L	b-L	a-L
15. Whatman paper	L*	65.58 (0.93)	65.48 (1.05)	65.63 (0.71)	65.85 (0.83)	70.48 (0.59)	70.19 (0.61)	70.44 (0.46)	72.77 (0.59)
	a*	-11.90 (0.31)	-11.23 (0.33)	-11.80 (0.32)	-11.30 (0.23)	-10.97 (0.14)	-10.35 (0.12)	-11.04 (0.14)	-10.97 (0.16)
	b*	-23.22 (0.55)	-24.43 (0.53)	-23.45 (0.76)	-24.74 (0.95)	-20.29 (0.38)	-20.26 (0.37)	-20.28 (0.84)	-17.28 (0.81)
17. Silk	L*	23.95 (0.39)	23.9 (0.35)	24.04 (0.43)	24.63 (0.83)	23.91 (0.27)	23.78 (0.27)	24.45 (0.59)	33.18 (0.47)
	a*	3.45 (0.26)	3.63 (0.19)	3.33 (0.21)	2.54 (0.23)	3.27 (0.19)	3.29 (0.22)	3.09 (0.2)	-10.41 (0.33)
	b*	-24.27 (0.35)	-24.42 (0.39)	-24.33 (0.68)	-25.06 (0.95)	-24.33 (0.24)	-24.05 (0.46)	-24.76 (0.33)	-24.02 (0.27)
18. Silk	L*	23.62 (0.38)	23.72 (0.46)	23.65 (0.35)	24.17 (0.3)	24.46 (0.62)	24.18 (0.52)	24.64 (0.39)	32.76 (0.53)
	a*	3.02 (0.2)	2.84 (1.14)	2.86 (0.14)	1.86 (0.67)	3.11 (0.17)	3.05 (0.19)	3.23 (0.13)	-9.89 (0.36)
	b*	-24.30 (0.48)	-24.42 (0.46)	-24.30 (0.28)	-24.89 (0.24)	-23.96 (0.32)	-23.49 (0.27)	-23.51 (0.52)	-23.46 (0.22)
19. Cyanotype	L*	26.92 (0.64)	27.06 (0.67)	28.47 (2.16)	30.58 (1.71)	27.7 (0.95)	28.74 (1.97)	29.45 (0.78)	46.65 (1.15)
	a*	-1.27 (0.58)	-1.25 (0.4)	-1.86 (0.45)	-3.46 (0.64)	-1.84 (0.56)	-2.54 (0.71)	-2.51 (0.41)	-13.19 (0.5)
	b*	-21.72 (0.34)	-21.75 (0.35)	-22.45 (0.59)	-22.12 (0.76)	-22.47 (0.64)	-25.11 (0.53)	-23.53 (0.37)	-17.08 (0.38)

(Continued)

Continued.

Sample		Control		Treated		Control		Treated	
		b-D	a-D	b-D	a-D	b-L	a-L	b-L	a-L
20. Cyanotype	L*	27.23 (0.24)	26.9 (0.46)	27.63 (0.25)	29.18 (0.3)	27.07 (0.5)	28.29 (0.47)	27.96 (1.25)	42.78 (1.48)
	a*	-1.41 (0.16)	-1.05 (0.15)	-1.81 (0.19)	-3.19 (0.17)	-1.33 (0.28)	-2.10 (0.24)	-1.67 (0.67)	-12.52 (0.29)
	b*	-21.73 (0.16)	-21.35 (0.32)	-22.19 (0.27)	-22.15 (0.23)	-21.47 (0.27)	-23.62 (0.2)	-21.78 (0.66)	-16.51 (0.42)
21. Wool	L*	31.73 (0.18)	32.15 (0.27)	32.31 (0.34)	32.74 (0.32)	32.15 (0.32)	32.68 (0.32)	32.4 (0.32)	32.7 (0.23)
	a*	-2.44 (0.15)	-2.26 (0.14)	-2.46 (0.15)	-2.26 (0.19)	-2.41 (0.15)	-1.15 (0.1)	-2.53 (0.05)	-1.63 (0.06)
	b*	-24.85 (0.16)	-25.23 (0.21)	-25.17 (0.15)	-25.52 (0.23)	-25.07 (0.11)	-26.94 (0.12)	-24.96 (0.13)	-26.35 (0.07)
22. Wool	L*	32.47 (0.35)	32.9 (0.15)	32.43 (0.21)	32.8 (0.19)	32.35 (0.28)	32.7 (0.39)	32.41 (0.56)	32.78 (0.38)
	a*	-2.62 (0.14)	-2.46 (0.13)	-2.69 (0.15)	-2.50 (0.14)	-2.68 (0.04)	-1.37 (0.08)	-2.59 (0.17)	-1.73 (0.12)
	b*	-25.11 (0.07)	-25.46 (0.21)	-24.77 (0.55)	-25.46 (0.21)	-24.81 (0.16)	-26.90 (0.16)	-25.01 (0.28)	-26.38 (0.29)
23. Wool	L*	27.22 (0.42)	27.47 (0.55)	27.25 (0.34)	27.35 (0.24)	27.12 (0.37)	27.15 (0.33)	26.87 (0.17)	27.16 (0.13)
	a*	-6.06 (0.21)	-6.07 (0.22)	-6.02 (0.07)	-6.06 (0.13)	-6.04 (0.09)	-5.43 (0.12)	-5.95 (0.08)	-5.58 (0.13)
	b*	-20.64 (0.28)	-20.69 (0.32)	-20.65 (0.14)	-20.80 (0.17)	-20.52 (0.12)	-21.42 (0.11)	-20.81 (0.16)	-21.30 (0.15)
24. Wool	L*	27 (0.2)	27.2 (0.28)	26.92 (0.16)	27.3 (0.22)	26.7 (0.32)	27.08 (0.11)	27.23 (0.42)	27.53 (0.33)
	a*	-6.01 (0.14)	-6.03 (0.1)	-5.86 (0.06)	-5.95 (0.08)	-6.07 (0.06)	-5.44 (0.04)	-6.07 (0.11)	-5.73 (0.1)
	b*	-20.70 (0.19)	-20.72 (0.22)	-20.57 (0.19)	-20.75 (0.22)	-20.72 (0.24)	-21.50 (0.29)	-20.70 (0.15)	-21.33 (0.12)

Note: Averaged colorimetric readings for each sample, before (labeled **B**) and after exposure (labeled **A**) to dark (**D**) or light (**L**), and where L* ranges from 0 (black) to 100 (white), a* from 127 (red) to -127 (green), b* from 127 (yellow) to -127 (blue).