The Role of the Substrate in the Fading and Reversion Behaviour of Prussian Blue Dye

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Introduction:
The pigment Prussian blue (ferric ferrocyanide) is known to exhibit phototropic behaviour due to its isotropic structure. Under prolonged exposure to light or in the absence of oxygen, Prussian blue will fade to Prussian white as its ferric iron is reduced to the lower oxidation state of ferrous iron.

\[ \text{Fe}^{3+} \cdot \text{Fe}^{2+} \cdot \text{CN}_3^{-} \neq \text{Fe}^{3+} \cdot \text{Fe}^{2+} \cdot \text{CN}_3^{-} \]

The compound will revert back to Prussian blue when re-exposed to dark, ambient conditions. Prussian blue dye was of common use during the nineteenth century. This study analyses the role of the substrate in the fading and reversion of Prussian blue dye by measuring the degree and rate of Prussian blue fading and reversion across samples of different substrates (cotton and silk). Determining the degree and rate of colour change of Prussian blue dye on different substrates will yield significant information that could help refine more specific display guidelines for artifacts, as well as quantify the risks involved in the anoxic treatment of Prussian blue textiles.

Experimental:

- Samples of cotton, silk, aged cotton, and aged silk were dyed according to an adapted 19th century tub dyeing recipe.
- Samples were faded for 20 days in a light chamber with an LED light source (100 kilolux).
- Samples of each substrate type were faded both in ambient conditions as well as under anoxia. A small anoxic chamber was constructed using Escal® barrier film and RP-K oxygen scavengers.
- Colour change was monitored using a spectrophotometer and calculated by the CIE 2000 L*a*b* formula.
- Further testing was done using a portable microfade tester with a xenon-arc light source (7 megalux).

Results and Discussion:

- All samples underwent visible fading. Microfading data (fig. 6) suggests that all samples would undergo visible colour change (dE 1.5) within roughly 2.5 months if exhibited continuously at 100 lux (a full study is necessary to determine how reversion cycles would affect this fade rate).
- Silk samples underwent significantly more rapid overall colour change than cotton samples.
- Silk samples exposed in the LED light chamber decreased in L* values, indicating an unexpected overall darkening rather than fading. This darkening was not observed in samples exposed by microfading.
- Fading rates were more consistent between sample types faded in anoxic conditions than between sample types faded in air.
- Fading and reversion rates are not reciprocal: a 20 day reversion period in dark, ambient conditions did not return the faded samples to their original colours.
- The majority of observed reversion occurred during the first 2 days of the 20 day reversion period.

Conclusions:

- Fading results confirmed that the substrate plays a role in the fading behaviour of Prussian blue dye when exposed to light in ambient conditions. The substrate appears to be less significant in the fading of Prussian blue dye under anoxic conditions. This could indicate a difference in the reaction mechanism when Prussian blue is reduced in anoxia.
- Further study is necessary to understand reversion behaviour, as the results of this experiment indicate that the rate of Prussian blue reversion is not reciprocal to its rate of fading. Specifically, cycles of fading and reversion should be explored.
- The experiment demonstrated a discrepancy in results between silk samples exposed to microfading and silk samples exposed in the LED light chamber, suggesting that the intensity of the light source has an effect on the reduction behaviour of Prussian blue on silk (rather than overall dosage alone). This is a significant factor to consider if constructing future experiments that seek to mimic museum exhibition lighting conditions.

Fig. 1. An example of a Prussian blue printed textile

Fig. 2. Samples being dyed by successive baths of iron (III) nitrate, potassium ferrocyanide, and alum solutions.

Fig. 3. Ambient and anoxic sample sets fading in the LED light chamber.

Fig. 4. Prussian blue being formed in solution

Fig. 5. Prussian blue prints and reversion of Prussian blue in cotton. All samples exhibited visible colour change (dE 1.5) within the first two minutes of fading.

Fig. 6. Microfading in air. Overall colour change (dE'94) of samples faded in ambient conditions (52% RH). The fading rate of Prussian blue on silk roughly doubled the fading rate of Prussian blue on cotton. All samples exhibited visible colour change (dE 1.5) within the first two minutes of fading.

Fig. 7. Microfading and reversion in anoxia for new cotton and silk. Overall colour change (dE'94) of samples in air and anoxia. For reversion, light exposure was interrupted for 10-20 minutes and resumed. The results showed that the rate of colour change is greater in anoxia for both cotton and silk. In air, colour reversion is observed, in anoxia, no reversion is observed.

Fig. 8. Spectral curve of silk sample before fading, after 20 days of LED fading, and after 20 days of reversion.

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