

Original research or treatment paper

Photochemical colour change for traditional watercolour pigments in low oxygen levels

Andrew Lerwill^{1,2}, Joyce H. Townsend¹, Jacob Thomas^{1,3}, Stephen Hackney¹, Charlotte Caspers^{1,4}, Haida Liang⁵

¹Conservation Department, Tate, London, UK, ²Image Permanence Institute, Rochester Institute of Technology, Rochester, NY, USA, ³Department of Conservation, University of Gothenburg, Sweden, ⁴Stichting Restauratie Atelier Limburg, Maastricht, Netherlands, ⁵School of Science and Technology, Nottingham Trent University, Nottingham, UK

An investigation for light exposure on pigments in low-oxygen environments (in the range 0–5% oxygen) was conducted using a purpose-built automated microfademeter for a large sample set including multiple samples of traditional watercolour pigments from nineteenth-century and twentieth-century sources, selected for concerns over their stability in anoxia. The pigments were prepared for usage in watercolour painting: ground and mixed in gum Arabic and applied to historically accurate gelatine glue-sized cotton and linen-based papers. Anoxia benefited many colorants and no colorant fared worse in anoxia than in air, with the exception of Prussian blue and Prussian green (which contains Prussian blue). A Prussian blue sampled from the studio materials of J.M.W. Turner (1775 – 1851) was microfaded in different environments (normal air (20.9% oxygen) 0, 1, 2, 3.5, or 5% oxygen in nitrogen) and the subsequent dark behaviour was measured. The behaviour of the sample (in normal air, anoxia, and 5% oxygen in nitrogen) proved to be consistent with the 55 separately sourced Prussian blue samples. When exposed to light in 5% oxygen in nitrogen, Prussian blue demonstrated the same light stability as in air (at approximately 21°C and 1 atmosphere). Storage in 5% oxygen is proposed for ‘anoxic’ display of paper-based artworks that might contain Prussian blue, to protect this material while reducing light-induced damage to other components of a watercolour, including organic colorants and the paper support.

Keywords: Accelerated aging, Light aging, Microfading, Lightfastness, Watercolour pigments, Anoxia, Hypoxia

Introduction

The display of light-sensitive materials leads to photo-oxidation in most cases, and it is therefore necessary for museums to achieve a balance between public access and preservation. It is well understood that traditional watercolours on paper are likely to comprise a number of colorants sensitive to photo-oxidation, which in a given work might include red and yellow laked organic pigments; a small number of inorganic pigments; organometallic materials such as Prussian blue; and a number of organic dye-based colorants such as indigo, gamboge, and others, with the common characteristic of being extremely difficult to detect non-destructively *in situ* without an exceptionally well-equipped laboratory and considerable resources. Assessments of light sensitivity have therefore been based on judgment and a knowledge of the

exhibition history of an artefact. The common preservation policy of restricting the display of works of art on paper assessed as light sensitive is applied at Tate, by agreeing that such works may be displayed only in low lighting (50–80 lux with no ultraviolet exposure), and for a maximum of two years in four (monitored by location). This often requires separate display spaces for light-sensitive works and can create difficulties for multi-venue exhibitions (previously displayed works may have to be substituted at later venues), and potential display conflicts if a loan has used up the allowable light exposure in advance of a key display in-house.

Another approach is to apply an objective means of assessing the light sensitivity of all the visually distinct colorants in a work of art, and to develop a display policy for each individual work based on the results (Ashley-Smith *et al.*, 2002; Ford & Smith, 2011), which Tate is in process of doing (Townsend *et al.*, 2013). To this end, a microfademeter was developed by Whitmore *et al.* (1999, 2000) and Whitmore

Correspondence to: Andrew Lerwill, Rochester Institute of Technology/IPI, 70 Lomb Memorial Drive, Rochester, NY 14623-5604, USA. Email: ajlpph@rit.edu or Joyce Townsend, Conservation Department, Tate Britain, Millbank, London SW1P 4RG, UK. Email: joyce.townsend@tate.org.uk

(2002) and has been improved, developed, and used by others worldwide (Ford, 2009; Druzik & Pesme, 2010; del Hoyo & Mecklenburg, 2011a, Liang *et al.*, 2011), as well as being developed for improved portability and automated use as a screening device (Lerwill *et al.*, 2008; Lerwill, 2011) as will be described here.

This study formed one strand of an extensive project on the practical application of anoxic framing to materials significant for the collections of British watercolour painting and also modern and contemporary art at Tate, London, where the work was carried out. Concurrent investigations were undertaken by Thomas (2012) into means of assessing the better preservation of paper in low-oxygen environments compared to its display in air, which comprises 20.9% oxygen. This developed into an assessment of the light sensitivity of some traditional watercolour pigments on a variety of substrates, and Prussian blue, for traditional, handmade, gelatine-sized papers of the type used by watercolour artists in the most significant period of British watercolour painting *ca.* 1750–1850 (Thomas *et al.*, 2010). The two strands of experimentation were carried out on the same sample sets, largely prepared in-house, while two other strands of the project then and later were focused on the quantitative measurement of oxygen levels close to 0% in sealed enclosures, and on developing a frame design that would retain the fill gas (nitrogen with a small percentage of oxygen, pure nitrogen, or pure argon) for a period of months or years (<http://www.tate.org.uk/search/anoxia>).

The emphasis on traditional watercolour pigments was justified by their importance in Tate's collection, which includes over 37 000 works on paper (though not all are coloured) by J.M.W. Turner (1775–1851), and some 4000 works on paper by other watercolourists, dating from *ca.* 1750–1850. Earlier research into the materials and techniques of J.M.W. Turner, using his studio materials at Tate, a resource unique for British art at this period, had shown that he regularly employed the great majority of the known artists' pigments available, invented, and improved over his long working life, in watercolour as well as in oil medium (Townsend, 1993, 1996, 2007). Thus, knowledge of the way his materials – or historically accurate reconstructions of his materials – respond to anoxia (0% oxygen) and hypoxia (defined here as 5% oxygen)¹ would be directly applicable to many other works in the collection, and by extension to many other artefacts painted with watercolour during this period or earlier: botanical illustrations, scientific illustrations, maps, etc. Much of the information gained can also be applied with reasonable

confidence to works made in the second half of the nineteenth century. Other studies have examined a limited number of such pigments, generally with a single sample of each (Korenberg, 2008; del Hoyo & Mecklenburg, 2011b; Beltran *et al.*, 2012).

A known concern with anoxic framing for artists' pigments and some other artefacts is Prussian blue, which has been observed to lose colour in the absence of oxygen, then regain most but not all of its colour on re-exposure to air (Russell & Abney, 1888; Beltran *et al.*, 2008; Korenberg, 2008; del Hoyo & Mecklenburg, 2011a; Beltran *et al.*, 2012). This phenomenon is known as phototropy, but the time for this reversion in relation to the time to lose colour is rarely discussed. The same effect has been observed in strong light, in air, followed by storage in the dark (Ware, 1999). Prussian blue is also reported to lose colour in sealed containers by reduction due to lack of oxygen (Ware, 1999), and when in proximity to reducing materials (Berrie, 1997). Reports of fading of Prussian blue pigment in light in the presence of normal air and/or nitrogen have been summarized (Kirby, 1993; Kirby & Saunders, 2004) as has similar behaviour when it is used as a textile dye (Rowe, 2004). Complete colour loss in 100% hydrogen environments was noted by Russell and Abney (1888).

The chemistry of 'Prussian blue' has been summarized elsewhere (Kirby & Saunders, 2004; del Hoyo & Mecklenburg, 2011a). It is a type II mixed valence transition metal complex: ferric ferrocyanide, iron (III) hexacyanoferrate (II) conventionally represented as $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot n\text{H}_2\text{O}$ (where $n = 14\text{--}16$). This is known as 'insoluble' Prussian blue. The formula quoted by Berrie (1997) could be considered more correct: $\text{M}^{\text{I}}\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6 \cdot n\text{H}_2\text{O}$, where M^{I} is a potassium (K^+), ammonium (NH_4^+), or sodium (Na^+) ion (depending on the method of manufacture), and $n = 14\text{--}16$. The potassium-containing variant is known as 'soluble' Prussian blue. In fact substitution of M can occur readily in aqueous media, and it is debatable whether the water used in manufacture, accidental damage such as flooding, or washing treatments for paper artefacts with Prussian blue might alter the expected formula during manufacture and use. Prussian blue can be precipitated from aqueous media as iron (II) hexacyanoferrate(II) as Prussian white or Berlin white, which is then oxidized to Prussian blue. The colour arises from charge transfer transition between two valence states Fe^{II} to Fe^{III} (Ware, 1999). Colour change due to light exposure is the result of more than one degradation pathway: these include a rapid and reversible reaction and hypothetical irreversible reaction(s) towards a more grey/yellow tone.

Prussian blue has been quite widely used in western painting, in both oil and watercolour, since the

¹Our definition. In other contexts hypoxia is defined as being below 15% oxygen for fire suppression, or the similar range of concentrations which harms human health.

mid-eighteenth century, and has been documented in Japanese prints (Leona & Winter, 2003) and Chinese, Indian, and other south-east Asian works of art from the nineteenth century (Bailey, 2012). It has been used as a textile dye between the early nineteenth and the late twentieth century (Rowe, 2004), and in traditional printing and lithographic inks until inkjet printing (for which it is not suitable) came to predominate in the later twentieth century (Townsend *et al.*, 2008). Images created via the cyanotype process contain Prussian blue: images of botanical samples for example, while plans and architectural drawings were copied as 'blueprints' by the same process from the mid-nineteenth century until the mid-twentieth century. The presence of Prussian blue has been reported (Korenberg, 2008) as precluding anoxic display and/or storage and the benefits anoxia could offer to other components of such artefacts. The detection of Prussian blue in the early periods of use is possible with reasonable certainty by using false colour infrared imaging, but by the twentieth century its distinction from a greater number of available blue pigments would require a combination of several imaging and non-destructive analytical methods. Investigation of safe parameters for its storage in modified atmospheres was therefore worthwhile.

The first serious investigation into the factors affecting the degradation of artists' materials was carried out for the 1888 British *Report on the Action of Light on Watercolours* (Russell & Abney, 1888), discussed later by Brommelle (1964), wherein they investigated the effects of light exposure on pigments under vacuum and in hydrogen, which in effect means in anoxic conditions. They noted the instability of Prussian blue, and of several other colorants, mainly organic ones. This and other publications relevant to anoxic storage of collections were summarized recently (Townsend *et al.*, 2008). It is a common feature of many reports on pigment behaviour in anoxia that the level of anoxia or degree of vacuum was not quantified, and neither were the pigments all independently analysed, nor given a solid provenance. Many would seem to have been contemporary with the period of the investigation, rather than historic samples. The study reported here addressed both these issues with rigour.

Selection and preparation of samples

The colorants for this survey were selected by pooling: information on every pigment reported as having some sensitivity to anoxia; Turner's known pigment usage up to 1850; knowledge of pigments with reports of anomalous fading in strong light including laser irradiation (many of these are semiconductors, like zinc white and the cadmium yellows); and adding

any whose manufacture or fading involves redox chemistry (such as indigo and logwood). Then, a variety of historical examples was sought out as a major component of a masters project in conservation, with an emphasis on materials history (Caspers, 2008), for which surviving English watercolour recipes used by the colourmen Winsor & Newton and Roberson were examined and collated, to create historically accurate reconstructions of nineteenth-century watercolour paint ground in gum Arabic, diluted with distilled water and applied as a wash onto paper. The paper used was specified and created for the project (Thomas, 2012), to simulate the white papers often used by Turner and his contemporaries: gelatine-sized and gelatine-glazed paper containing approximately 60% lincell (cellulose from flax) and 40% long cotton linter, made at Ruscombe Mill, France.

Samples were applied with a brush at four different densities. An area with even coverage and of a mid-tone was removed with a hole-punch, placed face-down in a 96-well plate and held there with loosely packed cotton wool, to form an 'organic and inorganic colour' set and a 'Prussian blue' set, each comprising samples with as wide a range of manufacturing dates and countries as possible. Sample codes are included below (based on the donor institutions listed in the acknowledgements) under results, since many samples when collected had a label that was not informative or even unique, e.g. 'Prussian blue' or 'red lake' stated in either English or Dutch, or simply a colour description such as 'blue' in a few cases.

The historical pigment samples were provided from a variety of sources, and their age was broadly known (see Tables 1–3). All samples were screened by examining them in ultraviolet light at $\times 100$ – 200 , then using scanning electron microscopy with energy-dispersive X-ray analysis (EDX) to check whether the composition was likely to match the label, and whether extenders were present. Anomalous samples and those with a high proportion of extenders were rejected. Prussian blue and Prussian green samples were analysed with Fourier transform infrared spectroscopy (FTIR) as well. In a few cases, these particular screening methods are not useful, e.g. for sepia, indigo, or logwood. In these cases, examples that both matched published FTIR spectra and had plausible EDX spectra were used, while less consistent samples of the same name were rejected from the set. Strenuous collecting efforts mostly led to at least three samples for each pigment sought, and to 55 samples in the case of the 'Prussian blue' sample set, ranging in date from mid-nineteenth century to the present. The Prussian blue samples therefore included both 'traditional' examples which have large, plate-like particles, and the fine-grained type obtainable today.

Table 1 Organic colorants (excluding Prussian blues)**

Pigment type	Well characterized?	Summary of behaviour	Pigment name	Code	Approximate date	ΔE_{ab}^* after microfading		
						Air average	Hypoxia average	Anoxia average
Brazilwood, presumably not laked	No, but UV and FTIR are consistent	Not permanent (Padfield & Landi, 1966)	Brazilwood	RK8	Made 2006	0.5	0.7	1.1
		Benefits from anoxia	Brazilwood, BR12	NG9	Made 2005	4.7	3.1	1.9
		Benefits less from hypoxia	Brazilwood and madder	RC-ICN-BM	2003	5.3	3.8	2
Cochineal lake	No, but provenance good	Benefits from anoxia	Logwood lake [misnamed] Cochineal lake	NG10 NGCD 1b	Made 1972 Made 1991	2.4 0.9	1.6 0.3	1.6 0.2
		Benefits less from hypoxia	Cochineal on Al-based substrate	RC-ICN-C1	Made 2003	1.3	0.6	0.2
Carmine	No, but, lack of UV fluorescence implies it is not a madder	Samples too stable to assess	Cochineal lake Carmine extra on Al/Ca-based substrate	NG C8 D&C 8/08	Made 1993 1862 or earlier	1.7 0.5	0.6 0.4	0.4 0.4
Kopp's purpurine	Synthesized from <i>Rubiaceae</i> sp. (madder)	Samples too stable to assess	Carmine on Al-based substrate Kopp's purpurine on alumina	OH13 RC-ICN-M2	19th-20th century 2003	0.6 0.7	0.5 0.2	0.5 0.2
Madders on various substrates	UV fluorescence implies madder	Most samples too stable to assess	Rose madder on Al-based substrate	RK9	pre-1982	0.3	0.7	0.1
	TTB samples previously analysed (Townsend, 1993)	TTB rose-coloured madder benefits from anoxia more than hypoxia	Brown madder on Sn-based substrate Brown madder on Fe/Ca/Si-based substrate	TTB 16 TTB5	c. 1830-51 c. 1830-51	0.4 0.5	0.7 1	0.7 0.3
			Madder on Al/Cu-based substrate	TTB4	c.1830-51	0.5	0.5	0.3
			Madder on Al-based substrate	RK6	Made 2002	0.5	0.5	0.3
			<i>Garance cerise</i> (cherry-coloured madder) on Al-based substrate	D&C 8/02	1862 or earlier	0.7	0.7	0.6
			Scarlet madder on Al/Cu/Fe-based substrate	TTB1	c.1830-51	0.8	0.8	0.5
			Madder carmine on Al-based substrate	TPC6	c.1930-80	0.8	0.8	0.5
			Madder, rose colour, on Al-based substrate	TTB14	c.1830-51	2.4	1.2	0.5
			Madder, on Al-based substrate	TTB2	c.1830-51	0.5	0.5	0.1

Non-madder lakes, various	Absence of UV fluorescence implies not madder	Most samples too stable to assess	Fine lake (red)	CA18	c.1820	0.8	0.5
		2 benefit from anoxia	Crimson lake on Al/Sn-based substrate	TRR2	1890	0.9	0.9
			Green lake on Al-based substrate	TR5	1860s	0.9	0.8
			Brown/red lake on Al-based substrate	TR10	1860s	1.9	0.8
			Fustic lake (yellow) on Al-based substrate	NG7	Made 1972	2.6	1
Gamboge	Confirmed with FTIR	Most samples too stable to assess	Gamboge	RC ICN9	c. 1900–1950	0.2	0.1
		One benefits from anoxia only	Gamboge	TTB3	c. 1830–51	0.3	0.2
		Another had no benefit or harm, if any conclusion can be drawn	Gamboge	NG WC3	1796–1827	0.4	0.2
			Gamboge	NG1	c.1851	0.5	0.2
			Gamboge	TRS7	1910	0.9	1.1
			Gamboge	MB A3	pre–1945	1.1	0.5
Quercitron lake	No, but provenance good	BW2-4 (Feller, 1963)	Quercitron lake 1 on Al-based substrate	NG8	Made 1972	0.5	0.7
		Samples too stable to assess	Quercitron lake 2	NG Q2	Made 1972	0.6	0.9
			Ackermann's yellow	NG WC4	1796–1827	0.8	0.6
Weld	No, but provenance good	BW3 (Padfield & Landi, 1966)	Weld	RK2	Made 2000–07	0.4	0.3
		Benefits from anoxia	Weld	RK1	Made 2000	0.9	0.4
		Benefits less from hypoxia	Weld lake	NG3	1796–1827	2.6	0.8
			Weld	NG2	1796–1827	3.2	1.1
Buckthorn <i>Rhamnus</i> sp.		<i>Rhamnus saxatilis</i> and <i>Rhamnus utilis</i> BW1-2 (Padfield & Landi, 1966)	Buckthorn yellow	RK3	Made 2001	0.4	0.8
		Stability depends on substrate (Saunders & Kirby, 1994)	Buckthorn on Al-based substrate	NG B	c.1970s–1980s	0.8	0.8
		As watercolour pigment BW1-2 (Feller, 1963)	Buckthorn lake	NG5	Made 1993	0.8	1.4
		No benefit or harm from anoxia, if any conclusion can be drawn	Indian yellow	NG WC6	1796–1827	0.5	0.4
Indian yellow (genuine)	EDX showed Mg to be present, as indication of the genuine product	BW5-6 (Baer <i>et al.</i> , 1986)	Yellow lake	TTR7	1890	0.2	0.2
		Samples too stable to assess					
		One of the most stable natural dyes (Crews, 1987)					

Continued

Table 1 Continued

Pigment type	Well characterized?	Summary of behaviour	Pigment name	Code	Approximate date	ΔE_{ab}^* after microfading		
						Air average	Hypoxia average	Anoxia average
Sepia	No, but FTIR spectra consistent	BWS4-5 (Feller, 1963) Samples too stable to assess	Sepia 12 400	TPC10	c. 1930–80	0.6		0.6
			Sepia	RK15	pre–2003	0.7		0.4
			Sepia	CA12	c.1820	0.8		0.6
Bistre	No, but provenance good	No benefit or harm from anoxia, if any conclusion can be drawn	Bistre	NG	1796–1827	1	1.2	1.4
				WC9				
Sap green	No	No benefit or harm from anoxia	Sap green	OH1	20th century	2.8	2.8	3
			Sap green	RK4	Made 2006	1.4	1.4	1.7
			Sap green	RK5	Made 2003	2.9	3	3.6
			Sap green lake	NG11	Made 1989	0.7		0.8
			Green lake, includes Prussian blue	TPC8	c.1930–80	2.8	3.8	4.9
Prussian green which includes Prussian blue	Prussian blue component confirmed with FTIR		Prussian green	MB BA2	Pre–1945	0.4		0.4
			Prussian green	MB A2	c.1850	1.6	2.2	2.8
			Prussian green	CA1	c.1820	2.2	2.4	3.7
			Indigo	OH14	20th century	0.3		0.3
Indigo	Samples too stable to assess		Indigo 2 (natural)	IMEH1	20th century	0.4		0.2
			Indigo	TPC5	c.1930–1980	0.4		0.4
			Indigo	T3	1800–32	0.4		0.4
			Indigo (synthetic)	MB A6	c.1850	0.5		0.4
			Natural indigo	RC	c.1900–1950	0.7		0.2
				ICN3				

**All colour difference measurements after one hour of microfading, expressed in CIELAB1976 colour space. Measurement error is ± 0.36 (from drift and noise). All colour differences are calculated with respect to the initial colour of the sample.

Table 2 Inorganic colorants which showed a significant colour change**

Pigment type	Well characterized?	Summary of behaviour	Pigment name	Code	Approximate date	ΔE_{ab}^* after microfading		
						Air average	Hypoxia average	Anoxia average
Vermilion	EDX confirms vermilion likely	No benefit or harm from anoxia	C[hinese] vermilion	NG WC11	1796–1827	1.5	1.9	2.2
			Red [includes zinc white]	TR11	1860s	2	1.9	2.2
			Vermilion	T2	1800–32	2.2	2.1	2.4
			Vermilion	CA22	c. 1820	2.3	2.2	2.6
			Vermilion	MB A7	c. 1850	3.2	3.5	3.7
			Vermilion 4	RC ICN8	c. 1900–50	5	4.8	4.9
			Vermilion	TRR4	1890	5.1	4.9	6.2
			Orpiment red [realgar?]	CA20	c. 1820	2.1	1.3	1.6
			Kings yellow [orpiment]	NG WC13	1796–1827	2.2	2.7	2.6
			Orpiment (yellow)	CA13	c.1820	4.8	4.9	5.5
Chrome yellow (lead chromate)	EDX implied that the 'Indian yellow' must be lead chromate	Most samples too stable to assess	Chrome red	OH11		0.4		0.2
			Chrome clair	D&C 8/05	1862, or earlier	0.5		0.4
Vandyke brown	No	Widely reported to darken after light exposure	Chrome yellow	OH12	1809–1821 or 1809–1921?	0.6		0.5
			Mid chrome yellow	TTB12	c.1830–51	2	2	1.9
			Indian yellow	NG4	1965	0.3		0.4
			Van Dyke brown	TRS9	1910	1.4	1.5	1.6

**All colour difference measurements, after one hour of microfading, expressed in CIELAB1976 colour space. Measurement error is ± 0.36 (from drift and noise). All colour differences are calculated with respect to the initial colour of the sample.

Table 3 Prussian blue sample set**

Code	Approximate date	Prussian blue sample name	Air		Hypoxia		Air		Anoxia	
			ΔE_{ab}^* after microfading	ΔE_{ab}^* after 3 days reversion in air	ΔE_{ab}^* after microfading	ΔE_{ab}^* after 3 days reversion in hypoxia	ΔE_{ab}^* after microfading	ΔE_{ab}^* after 3 days reversion in air	ΔE_{ab}^* after microfading	ΔE_{ab}^* after 3 days reversion in anoxia
CA15	c.1820	Prussian blue	6.8	1	5.7	0.7	2.3	9.4	11.5	1.2
D&C 8/01	1862, or earlier	Blue de Prusse	1.7	0.7	1.6	1.6	0.8	1.5	3.5	2.1
HK1 1	pre-1985	Prussian blue	1.8	0.4	2.5	2.2	1.3	2.3	3.7	1.9
HK1 2	pre-1985	Prussian blue	2.1	0.2	2.5	0.6	0.5	2.4	2	1.3
HK1 3	pre-1985	Antwerp blue	3.4	1.9	3.2	2.1	1.4	2.5	4.6	1.2
HK1 4	1994	Prussian blue	2	0.6	2	0.4	0.5	1.3	1.3	1
HK1 5	1994	Prussian blue	1.1	0.4	1.7	0.7	1.8	1.4	1.4	1.4
MB 1	c.1820-1850	Prussian blue (Berlijns Blauw)	1.6	0.4	2.2	1.7	0.7	2.9	7.8	2.9
MB 2	c.1820-1850	Prussian blue (Berlijns Blauw)	1.3	0.5	1.6	0.5	1	1.6	2.8	2
MB 8	pre-1945	Prussian blue	3	0.7	2.2	0.7	0.5	3.9	7.5	2.6
MB A1	c. 1850	Prussian blue	0.7	0.5	0.9	0.3	0.3	2.1	3.4	1.3
MB A5	c. 1850	Antwerp blue	2.4	0.7	2.1	0.6	0.6	2.3	2.1	1.3
MB BA1	pre-1857	Prussian blue	1.7	0.3	5.3	0.4	1.2	8.8	8.9	2.9
NG 12a	1990s	Prussian blue	5.8	0.4	5.9	1.7	2.6	7.9	8.3	2.3
NG 12b	1990s	Prussian blue	10.7	1.4	7.8	0.5	0.5	11.3	12.4	1.5
NG AA (NG WC2)	1796-1827	Ackermann ' Antwerp blue	1.2	0.3	2.8	1.7	1	4.6	5.4	3.9
NG ALP	2000s	Prussian blue	2.5	0.1	3.1	1.5	1.7	3.9	2.6	2.4
NG AR	mid-19th century	Prussian blue	5.4	1.2	4.2	1.7	1.5	5.3	4.9	2.1
NG BA	1855	Good Berlin blue from Weimar	8.2	1.3	7.5	0.7	2.8	15.7	13.1	9.6
NG BB	1842	Berlin blue	4.2	1.5	3.9	1.5	1.3	3.3	7.5	4.3
NG BCB	mid-19th century	Prussian blue	2.4	0.5	3.9	1.7	1.3	2.3	3.4	1.8
NG GA	early 19th century	Prussian blue	6.2	0.4	9.2	0.2	0.5	12.8	11.8	1.9
NG JSM	1830-40	Prussian blue	8.3	0.1	6.2	1	1	10	9.2	0.9
NG K7	1990s	Prussian blue	1.6	0.2	2.5	1	1.3	3.1	3.3	1
NG MA	1805-17	Prussian blue	5.1	0.2	3.7	1.4	1.8	7.1	6.6	0.4

NG MB	18th century	Prussian blue	1.7	0.6	2.3	1.7	1.8	1.7	1.9	1.7	1.7
NG NB	mid-19th century	Blue	3.1	0.3	4.5	0.8	0.5	5.5	6.8	2	2
NG NP	mid-19th century	Prussian blue	2.4	1	3	1.1	1.8	5.2	5.4	1	1
NG OZ	1742–1810	Prussian blue	5.9	0.4	4	0.7	1.2	10.9	8.2	2.5	2.5
NG RA	1800–30	Prussian blue, barytes, gypsum	2.8	0.2	3.5	1.3	0.6	4.1	4.3	1.6	1.6
NG RC	1800–30	Prussian blue, gypsum	4.2	0.8	4.5	0.5	0.6	6.3	7.4	0.9	0.9
NG RD	1800–30	Prussian blue, kaolin, quartz	12.6	2.6	11.1	3.7	1.2	12.8	13.4	5.4	5.4
NG RE	1800–30	Prussian blue, barites	3.8	0.5	5.3	0.4	1.6	8	9.1	1.8	1.8
NG RG	1800–30	Prussian blue, barites	6.1	1.5	7.1	3.8	2	7.2	11.4	6.3	6.3
NG SA	2000s	Prussian blue	0.8	1.2	0.2	0.5	1.4	1.6	2.6	2.2	2.2
NG SB	2000s	Prussian blue	2.4	0.8	3.4	1.2	1.7	5.1	3.5	1.3	1.3
NG SC	2000s	Prussian blue	4.5	0.4	4.1	1	2.3	5.8	7.4	1.5	1.5
NG SD	2000s	Prussian blue	7.7	0.2	6.9	0.6	1	8.5	9.1	1.1	1.1
NG TB	n.d.	Turnbull's blue	0.9	0.5	1.4	0.5	0.5	1.8	2.7	1.9	1.9
NG VA	1770–1831	Prussian blue	8.5	0.5	7.1	1.6	1.6	10.6	9	0.5	0.5
NG VB	1770–1831	Prussian blue	4	0.6	3.5	1.7	1.7	7.1	5.5	1.2	1.2
NG WC1, (AP)	1796–1827	Prussian blue	2.9	0.3	4.4	0.6	1.1	5.2	5.2	0.8	0.8
NG WN	20th century	Prussian blue, alkalie ferric ferrocyanide	3.3	0.4	3.9	0.6	0.6	6.7	6.5	2.5	2.5
OH2	20th century	Prussian blue (Chinese Blue)	1	0.7	1.2	1.2	1.2	1.2	2.5	1.7	1.7
OH4	20th century	Prussian blue (Blue de Prusse)	1.1	0.3	2	0.7	0.9	2.3	1.8	1.2	1.2
OH6	early 20th century	Prussian blue (Parijs blauw)	1.5	0.3	1.7	0.5	0.5	1.4	1.3	0.3	0.3
OH8	20th century	Prussian blue (Mineraalblauw)	2.2	0.3	3.2	0.5	0.4	3.1	2.2	2.3	2.3
OH9	20th century	Prussian blue (ijzercyaan Berlijns blauw)	2.4	0.1	3.1	1	0.9	5	4.2	3.2	3.2
RC ICN1	c.1900–50	Prussian blue	5.2	0.7	6.5	1	0.6	8	7	0.7	0.7
RC ICN2	c.1900–50	Chinese blue	3.6	1.8	2.8	0.9	1.3	3.8	4.9	1.4	1.4

Continued

Table 3 Continued

Code	Approximate date	Prussian blue sample name	ΔE_{ab}^* after microfading		ΔE_{ab}^* after 3 days reversion in air		ΔE_{ab}^* after microfading		ΔE_{ab}^* after 3 days reversion in hypoxia		ΔE_{ab}^* after microfading		ΔE_{ab}^* after 3 days reversion in anoxia		ΔE_{ab}^* after another 3 days reversion in air	
			Air	Air	Air	Air	Hypoxia	Hypoxia	Anoxia	Anoxia	Air	Air				
RK14	pre-1962	Prussian blue	1.4	0.1	1.4	0.7	1.4	2.3	2.8	2.3	2.8	2.3	2.8	2.3	1.1	
T CA1	c. 1890-1950	Antwerp Blue	1.3	0.7	1.4	1.1	1.4	2.7	3.3	1.4	3.3	2.7	3.3	2.7	3.1	
T CA7	c. 1890-1950	Chinese Blue 23	1.7	0.5	1.8	0.8	1.8	1.7	2.2	1.8	2.2	1.7	2.2	1.7	0.6	
T RR1	1890	Prussian blue	0.9	0.3	2.6	1.6	2.6	1	3.7	1.6	3.7	1	3.7	1	2.6	
T1	1800-32	Prussian blue (Berlijns Blauw)	3.5	0.5	3	1.1	3	5.8	6.8	1.1	6.8	5.8	6.8	5.8	2.5	

**All colour difference measurements, colour space after one hour of microfading, expressed in CIELAB1976. Measurement error is ± 0.36 (from drift and noise). All colour differences are calculated with respect to the initial colour of the sample.

All samples coded 'TTB ...' are from J.M.W. Turner's studio pigments (Tate Gallery Archive 7315.7, Tate conservation archive Q04047) and were therefore particularly relevant to the institution's assessment of the potential benefit of anoxic storage. This collection appears to include materials purchased early and never fully used within his lifetime, but is likely to be biased towards his last decades, the 1830s and 1840s.

Initial, multiple, studies on the TTB pigments were done with dry pigment rubbed into Whatman cotton-based filter paper, to establish reasonable pigment density, exposure times, etc. Thereafter, all microfading was done on samples made up as historically accurate watercolours ground in Gum arabic, but referred to hereafter by the pigment name alone.

The National Gallery, London, supplied a collection of Prussian blue and lake paint-outs, previously prepared on high-quality paper as historically accurate reconstructions for experimental purposes (Saunders & Kirby, 1994; Kirby & Saunders, 2004), and therefore well characterized.

In all cases, the aim was to simulate watercolour paint as used by artists, rather than the pigment in isolation. Recent studies on textile dyes in particular have also aimed to simulate usage (Rowe, 2004; Beltran *et al.*, 2012).

Experimental method for microfadometry

Most microfadometers employ a high-powered continuous-wave xenon light source (in this case an Ocean Optics HPX2000). This is connected directly to a solarization-resistant optical fibre with a 600-micron fibre core. The end of this fibre is connected to a confocal probe designed for this task, containing two lenses (matched achromatic pairs optimized for the visible region). Light passes through an extended hot mirror to remove infrared radiation in order to reduce temperature, and ultraviolet radiation to mimic the museum environment. The filtered light is focused to a 0.25-mm spot.

In order to monitor colour change, scattered light from the small sample area is coupled back into the optical system via another optical probe of the same design at 45° to the normal. Sampled radiation then passes through a neutral density filter to avoid saturation of the fibre optic spectrometer detector. The spectrometer (Avantes Avaspec 2048) receives this signal via an optical fibre, and the software (AvaSoft 7.0) analyses change in the spectrum and the rate of fading. This instrument was discussed previously (Lerwill *et al.*, 2008).

A main source of systematic error was a combination of drift in the lamp and spectrometer (dominated by the drift in the spectrometer). Random

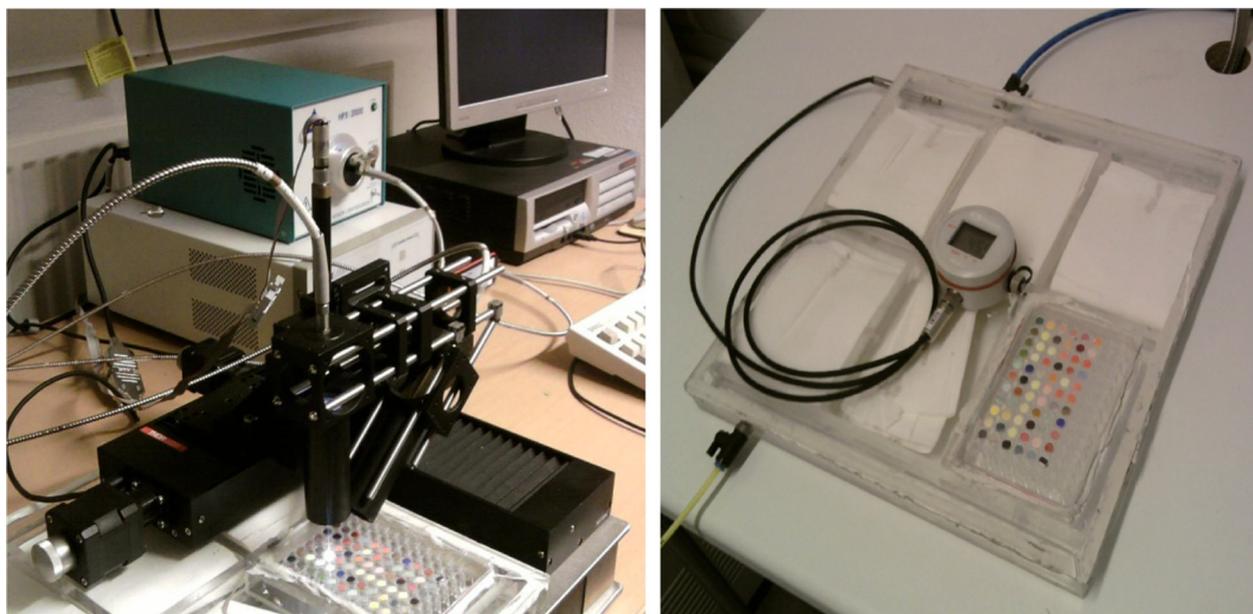


Figure 1 Left: The automated micro-fadometer system which controls movement of the probe head via the attached motorised XYZ stage. Right: a coloured set in the sample chamber.

noise is mainly due to photon noise (or shot noise associated with the photon arrival and detection probability) and thermal noise of the detector electronics (dark noise and readout noise). Over a seven-hour period of continuous running, these were found to contribute an error no greater than $0.36 \Delta E_{ab}^*$ which did not increase over seven days.

The well plates of samples were mounted in the roof of a Perspex[®] (Lucite International UK Ltd, Darwen, UK) chamber built in-house, flushed continuously with 100% nitrogen, or 1–5% oxygen and 99–95% nitrogen supplied premixed (Fig. 1). The purging gas was split such that a fraction flowed through a water bubbler and the rest directly to the controlled chamber; the portion running through each segment was then valve-regulated and the humidity of the resultant gas stream was measured using a Tinytag[®] (Gemini Data Loggers (UK) Ltd, Chichester, UK) humidity meter. Humidity remained within desirable limits of $40 \pm 5\%$ throughout the experimental process. In the case of microfading in air the valves were left open to allow air flow from the non-air-conditioned laboratory.

Three similar and separate fading runs were conducted at three different oxygen levels for the Prussian blue sample set. In air, anoxia or hypoxia, Prussian blue colour change was measured following a one hour (1.7×10^7 lux-hours) microfadometer exposure, then measured again after the set had remained in the same environment for three days, with continuous gas flushing. The sets that had been measured while housed in anoxia or hypoxia were exposed to air while they were kept in subdued light for another three days, then their colour was measured again with the microfading apparatus. This three-day recovery time was based on the reversion behaviour

of sample TTB6, Prussian blue from Turner's studio (Lerwill, 2011), following microfading in anoxia of multiple samples of the Prussian blue pigment, and monitoring for colour recovery in air over many days. Recovery stopped after 20–30 hours (see Fig. 5 to be discussed later). The recovery time in air was extended to a larger value of three days before measuring the reverted colour, to allow complete reversion if the samples varied in their properties. The microfadometer was left running over the three days to maintain positional and photometric calibration. Repeat measurements on the same locations were possible using the high positional repeatability of the XYZ stage.

The coloured sample set was similarly treated.

The reflectance spectrum for each sample was converted using the Commission International de l'Eclairage (CIE) 1976 $L^*a^*b^*$ equation for the 2° standard observer under standard illuminant D65. The $L^*a^*b^*$ values were then used to calculate colour difference for the samples in CIELAB (ΔE_{ab}) or CIE2000 (ΔE_{00}) for the same illuminant and 2° standard observer (CIE, 1986, 2001).

Results of colour change for one hour of fading (corresponding to an exposure of approximately 1.7×10^7 lux-hours over the focused spot) were analysed for all pigments. If a colour difference less than $\Delta E_{00} = 1$ was measured in both air and anoxia for this fade duration, the assessment of the pigment was discontinued since a colour change on this scale is statistically insignificant for comparison of behaviour in different atmospheres.

Pigments that showed a colour difference $\Delta E_{00} > 1$ in any atmosphere were further faded in oxygen concentrations of 0%, 5%, and air, with fades repeated three, three, and five times, respectively, to give

insight into the effects of measurement error (due to focusing) and sample non-uniformity (due to hand painting, varied particle size and resistance to fine grinding between samples).

Results and comparisons to other studies

Unpainted paper

Ruscombe mill paper, the gelatine-sized and gelatine-glazed substrate for the majority of samples, was microfaded without any pigment applied, and was found to be stable over 140 minutes (Fig. 2). Thus, it would not contribute to any colour change to watercolour paint applied to it, when microfaded for 60 minutes.

Coloured sample set

Sets of coloured samples were also microfaded in 0%, 5% oxygen and air for one hour. Subsequently, after three days in the same atmosphere in subdued light, the colour was measured using the microfadometer. Then after air exposure of three days, the colour was measured again. There was no reversion of lost

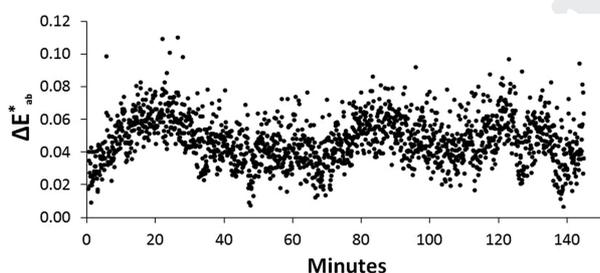


Figure 2 Microfading results over 140 minutes for gelatine-sized and glazed 'Turner white' Ruscombe mill paper without paint applied.

colour and no change following re-exposure to air. Therefore, only the colour change after one hour in each atmosphere is shown in Table 1 for the organic pigments, and Table 2 for the inorganic pigments which showed a colour change significantly higher than experimental error.

It should be borne in mind that all the samples comprised a composite system of cotton and linen-based paper, gelatine internal and external size, and pigment in gum Arabic medium. While behaviour is reported here in terms of pigment name for brevity, it must be emphasised that these results are not applicable to the same pigment on a different substrate such as acid paper or paper with an alkaline reserve, and are even less applicable to the same pigment bound in a different medium and possibly interacting chemically with it in some cases. Even equating them to the behaviour of the dry pigment in isolation (masstone or full colour) is an approximation.

For organic pigments (Table 1), brazilwood, cochineal, the single (Turner) madder, and the two non-madder lakes of unknown dye type, weld, and one gamboge among several more lightfast gamboge samples, all showed less colour change in anoxia than in air and the benefits, though less, were still observed in hypoxia. Sap green showed significant fading, to the same extent within experimental error, in air, hypoxia, and anoxia. Bistre and buckthorn showed barely significant colour change and no variation in behaviour in the three atmospheres. For example, brazilwood (Fig. 3, Table 1) and cochineal benefited from anoxia more than from hypoxia. The fading studies of Beltran *et al.* (2012) similarly showed that

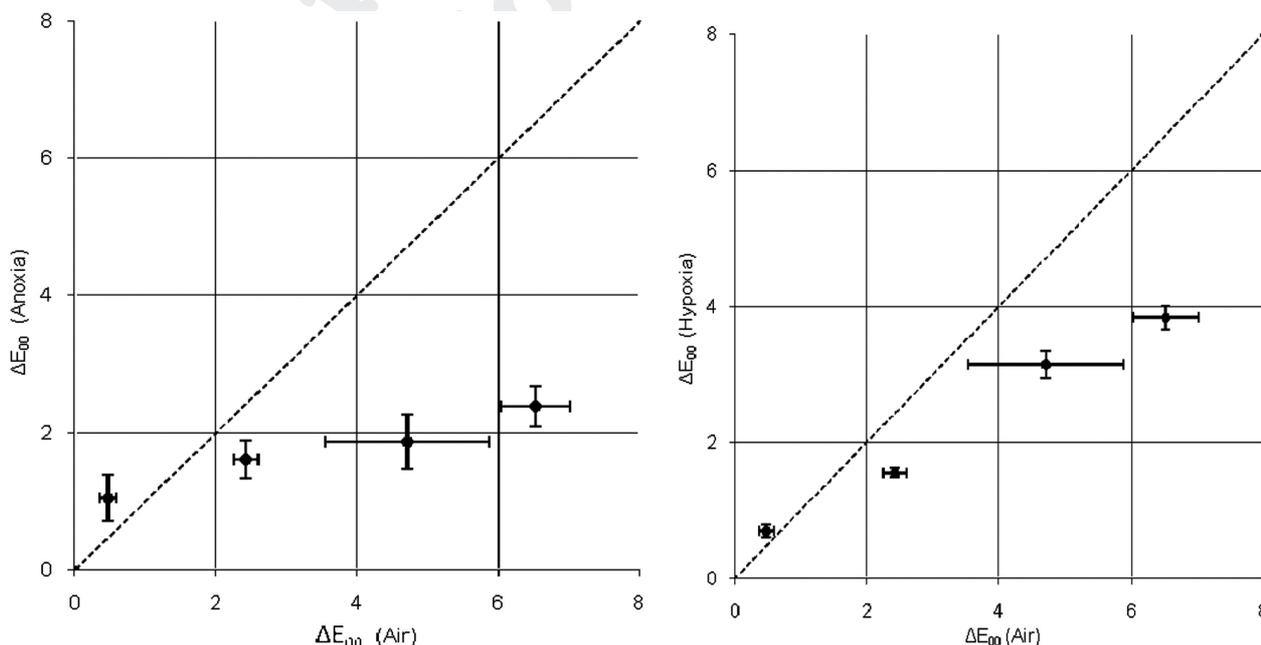


Figure 3 Colour difference for four brazilwood samples in air vs. anoxia immediately after microfading (left) and air vs. hypoxia likewise (right). Five repeat measurements in air and three in anoxia and hypoxia were performed and the averages are shown in the plot.

well-characterized samples of weld, buckthorn, madder, and brazilwood and other samples labelled sepia, yellow lake, and indigo also showed less colour change in anoxia than in air, sometimes much less.

The following organic pigments were too stable to show fading in air (this was predictable under the test conditions) and did not show any colour change in anoxia or hypoxia either, suggesting that within the limitations of our measurements they were not harmed by lower oxygen level environments: carmine, Kopp's purpurine, quercitron lake, genuine Indian yellow, sepia, and indigo.

Only a few inorganic pigments (Table 2) showed some colour change – which was also predictable (Weber, 1923). Orpiment/realgar and Vandyke brown altered sufficiently to suggest that they neither benefited nor were harmed by anoxia, as found also by Korenberg (2008) for orpiment. This suggests their fading is unaffected by the presence of oxygen. Vermilion changed colour considerably. It is known to be less excellent in terms of lightfastness than many inorganic pigments (Schaeffer, 2001) – with varied colour changes across seven samples, but showed neither benefit nor harm from anoxia. Such varied behaviour suggests that some vermilion samples used here might be contaminated or mixed, the former being entirely possible in the samples from used watercolour-boxes.

Several historic samples of inorganic pigments proved to be too stable for measurement of their behaviour in anoxia after one hour of microfading, despite reports of colour change in anoxia: two cadmium yellows, two emerald greens, two red iron

oxides, one burnt umber, one yellow ochre, three masticot samples, one red lead, one lead white, and one smalt. Most chrome yellow samples were similarly stable, with the exception of Turner's chrome yellow, which faded sufficiently to show that it benefited from anoxia or hypoxia.

Colour recovery of Prussian blue following microfading in anoxia or hypoxia

Typical colour recovery in air following microfading in anoxia for TTB6, Turner's Prussian blue, over approximately one day, is shown in Fig. 4, in CIELAB1976. TTB6 recovered colour in around one day, as seen in Fig. 5.

Microfading on TTB6 in 0, 2, 3.5, 5, 10, and 21% oxygen concentrations for fade durations of 15 minutes, one hour, three hours, and 15 hours was

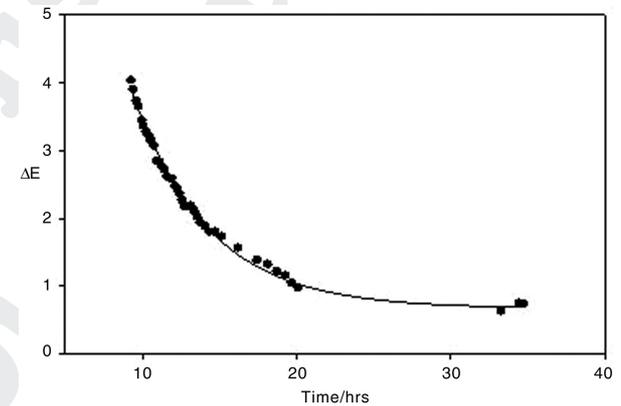
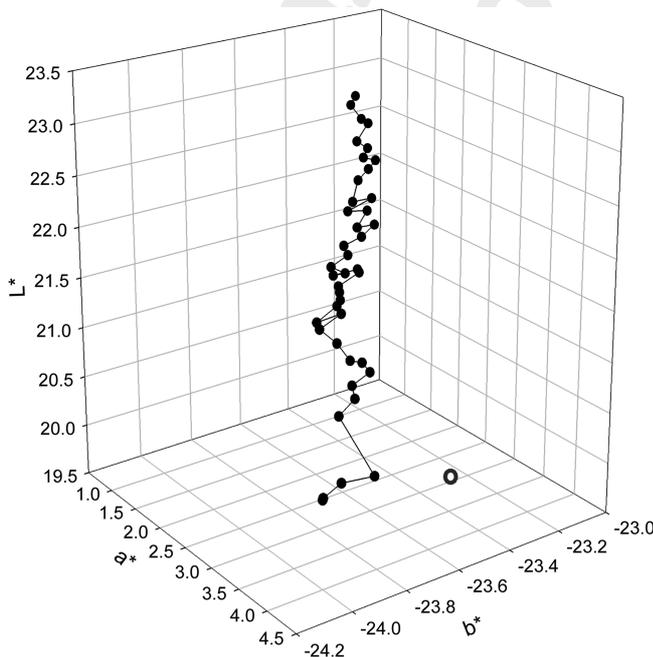


Figure 5 Time for colour reversion of TTB6. The y axis shows colour change with respect to the colour prior to microfading in air. The curve shows an exponential decay function.

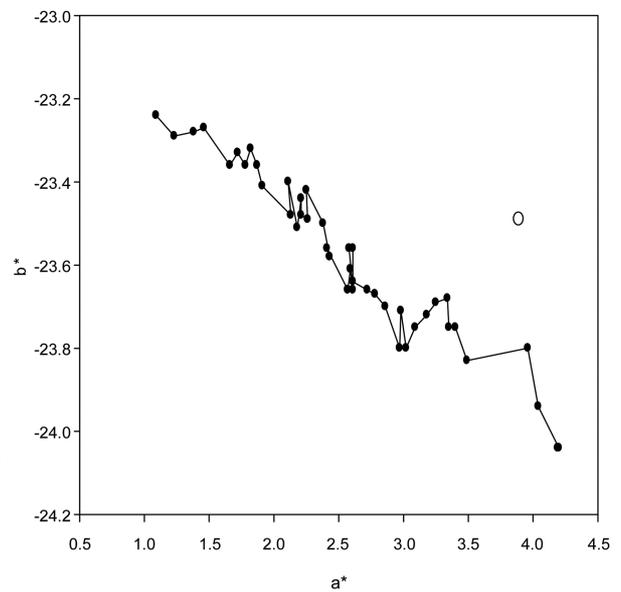


Figure 4 Turner's Prussian blue TTB6 reversion behaviour on re-exposure to air in minimal light in CIELAB1976 shown (left) with the open circle indicating the initial colour before microfading in anoxia, and the reversion path represented from top to bottom. Right: In the a* – b* plane the reversion is shown from left to right.

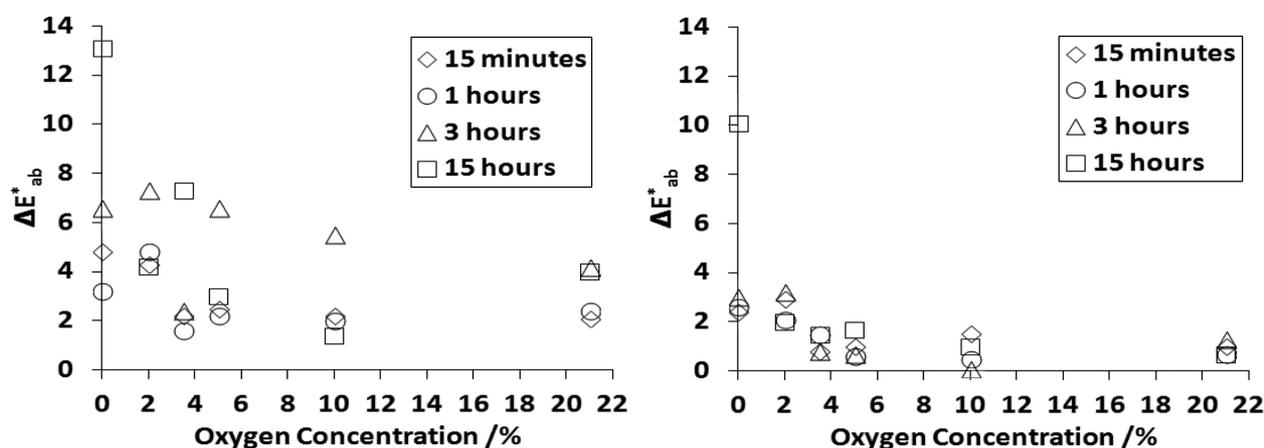


Figure 6 Microfading of TTB6 in 0, 2, 3.5, 5, 10, and 21% oxygen (left) and the measured colour after three days of colour recovery in the different oxygen concentrations (right).

conducted and colour recovery was monitored in each case. ΔE was found to increase with fade duration at all oxygen concentrations, and colour change typically reached a plateau or reduced after three hours of fading, when no blue colour remained. However, in anoxic conditions the colour difference due to microfading was greater than that seen at other oxygen levels (see Fig. 6). The colour change in anoxia after 15 hours, significantly greater than the rest, was repeatable over three runs and found to be consistent. This significant fading of Prussian blue to white in anoxia has been widely reported. Again the residual colour change after recovery was large in anoxic conditions when compared to colour recovery at other oxygen levels. The value of ΔE achieved after recovery in anoxia was repeatable, and agrees with previous reports that Prussian blue does not recover colour until exposed to oxygen (generally atmospheric oxygen levels).

Importantly it was found that the ΔE after recovery increases with decreasing oxygen concentration as shown in Fig. 6, with colour recovery (three days in air) less complete following microfading at 0 and 2% oxygen.

The 5% oxygen level (defined as 'hypoxia) used for the Prussian blue and colour sample sets was selected following this initial study, to prevent the greater colour loss observed in anoxic conditions. This in combination with the measurements on the Prussian blue sample set led to a patent application.²

Prussian blue sample set

The results detailed in Table 3 are summarized as histograms. Fig. 7 shows that after microfading in air the Prussian blue samples had a range of colour changes with the majority at $\Delta E_{ab}^* = \sim 2$. After colour recovery in air, this range was reduced.

²Patent EP2344347A1 published 20 July 2011 in the UK (filed 11 September 2009) and US20110168949 published 14 July 2011, by Stephen Hackney, Joyce H. Townsend, Jacob Llewellyn Thomas, and Andrew Lerwill on behalf of the Board of Trustees of the Tate Gallery, *A Method For Preserving Objects Containing Pigment*.

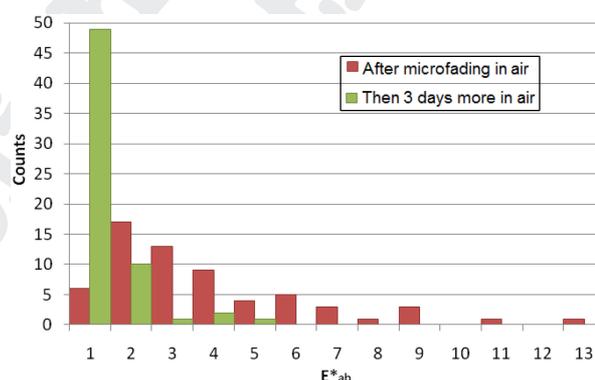


Figure 7 Colour difference for the Prussian blue sample set after fading in air (red), then after three days in low lighting to permit reversion (green). The histogram bin sizes are $1 \Delta E_{ab}^*$.

Fig. 8 shows that after microfading in anoxia, the samples had a range of colour changes similar to those faded in air. After storage in low light for three days in anoxia, the distribution of the colour changes had not changed significantly. However, after further three days storage in air, the range of colour changes from the initial colour was significantly reduced.

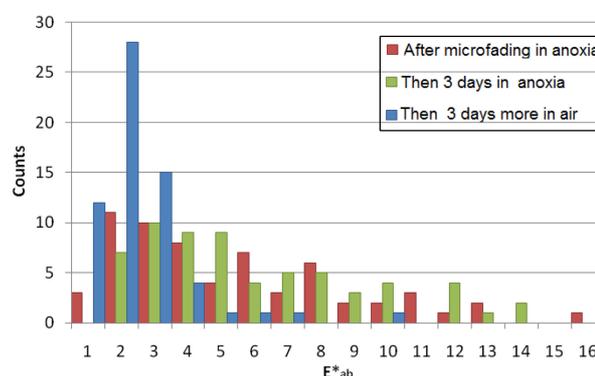


Figure 8 Colour difference for the Prussian blue sample set microfaded in anoxia (red) and after three days in anoxia in subdued light (green) and following this after re-exposure to air for 3 days in low light to permit colour recovery (blue). The histogram bin sizes are $1 \Delta E_{ab}^*$.

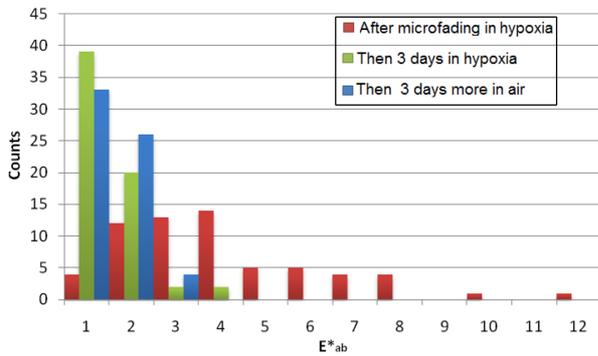


Figure 9 Colour difference for the Prussian blue sample set microfaded in 5% hypoxia (red) and after three days in hypoxia in low light (green) and following this after re-exposure to air for three days in low light to permit colour recovery (blue). The histogram bin sizes are 1 ΔE*ab.

Fig. 9 shows that after microfading in hypoxia, the samples had a range of colour changes similar to the range in anoxia (Fig. 7) and air (Fig. 8). After storage in hypoxia, the range was significantly reduced, but after further storage in air the distribution in colour change had not changed significantly. Figs. 7–9 demonstrate that Prussian blue fades rapidly in air, anoxia, and hypoxia, but colour recovery is significantly more effective in air and hypoxia. Further analysis of the data shows that a greater colour change was observed in the Prussian blue samples when faded in anoxia than in air, as expected (Fig. 10, top left). The lines at 45° in Fig. 10 represent no change in behaviour between the two atmospheres. Fading in hypoxia and air resulted in similar colour

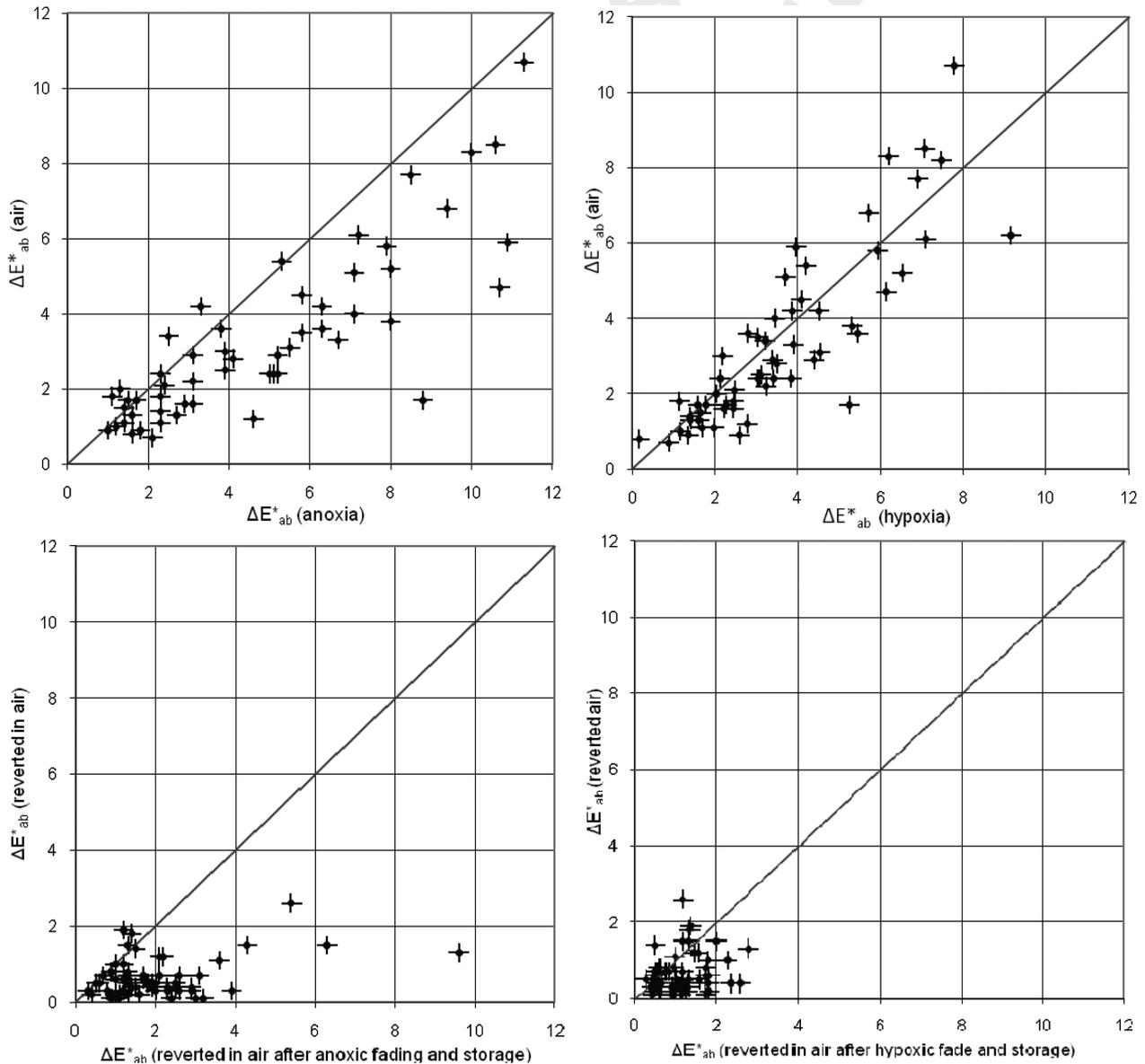


Figure 10 Colour difference for the Prussian blue sample set immediately after microfading for one hour in air vs. anoxia (upper left), and 5% hypoxia vs. air (upper right). Colour difference for the Prussian blue sample set after microfading and storage in air vs. fading and storage in anoxia with three days exposure to air afterwards (lower left). Colour difference after microfading and storage in air vs. microfading and storage in hypoxia with three days exposure to air afterwards (lower right).

changes as the data points in Fig. 10 (top right) are scattered evenly around the lines.

When the Prussian blue set microfaded in anoxia was re-exposed to air, a considerable degree of colour reversion occurred over the three-day period, but a number of Prussian blue samples did not revert fully (Table 1). This indicates that removing Prussian blues from anoxic display and exposing them to air in subdued light afterwards is not an appropriate strategy to secure better preservation of other components of an artefact that would otherwise benefit from anoxic conditions. But display in hypoxia avoids such permanent colour loss.

Prussian green

Prussian green can be made by two methods: by stopping the manufacturing process of Prussian blue at the stage when the sediment is green before adding hydrochloric acid to turn the pigment blue, or by combining Prussian blue with a yellow pigment such as yellow ochre or gamboge (Eastaugh *et al.*, 2004). These two techniques of production result in two fundamentally different products, one resulting in a compound the other in a mixture (respectively). The latter process was dominant and the former can be regarded as insignificant in terms of pigment manufacture (Harley, 2001). All the examples studied here included Prussian blue identifiable by FTIR, and they all had a yellow pigment whose presence was most easily detectable with optical microscopy. Results from the microfading of this sample set can be seen towards the end of Table 1.

The behaviour of these samples was the same as Prussian blue in all cases, and the same conclusions could be drawn as for Prussian blue; a conclusion mirrored in other aspects of this research (Lerwill *et al.*, 2013). There was little other colour change to indicate the behaviour of the (unidentified) yellow components.

Discussion and conclusions

This investigation by microfading of traditional watercolour pigment behaviour in anoxic conditions was the largest to date and in hypoxic conditions was the first to date. Results are encouraging for both the application of anoxic framing for display of traditional watercolours, and further research into the benefits of hypoxia using lower levels of illuminance for accelerated ageing. Beltran *et al.* (2012) recently published such a study on a large sample set of dry artists' pigments, and the same dyes in many cases on wool or silk, exposed to moderately accelerated light ageing below 8000 lux, and reported that the vast majority of their samples (including organic dyes on silk, organic pigments applied dry to paper, fluorescent dyes, and contemporary gouache) faded significantly less in anoxia or at the same rate as in air, with half of the small number of exceptions being Prussian blue samples.

The behaviour of Prussian blue in air, hypoxia, and anoxia has been investigated here, with emphasis on the 1–5% range of oxygen concentration, and its colour recovery in air following exposure to light in anoxic or hypoxic conditions was studied on a set of 55 samples, of which more than half were made in the nineteenth century or earlier, the rest having dates spanning the twentieth century. Photochemical changes in hypoxia at 5% oxygen were found to induce the same behaviour that the pigment shows in air, in all cases. Repeated microfading runs of the traditional Prussian blue used by Turner (TT6, dated to *ca.* 1830–51) showed that the same did not hold for 1% oxygen and only held sometimes for 2% oxygen, while 3.5% oxygen was comparable in effect to 5%. Thus, the use of 5% oxygen, styled 'hypoxia' here, has particular benefits when the object to be encapsulated is suspected from a knowledge of materials history to contain Prussian blue, or Prussian green made from Prussian blue and a yellow pigment, or when the absence of these materials cannot be proved with the resources to hand. The valid concern that anoxic storage and even more so anoxic display will lead to an irreversible colour loss in Prussian blue and Prussian green is thus avoided, while the paper substrate and the majority of other colorants would both suffer less photo-oxidation than in air, for the same light exposure.

Additionally, this result is a significant departure from the argument of Thomson (1965) that the rate of oxidative degradation of most organic pigments would show little or no decrease until an oxygen level of parts per million were achieved, a viewpoint backed up by artificial ageing experiments conducted by Leene *et al.* (1975). Alternatively Giles *et al.* (1956) argued that the photodegradation of most organic colorants decreases linearly with oxygen concentration, a claim which was backed empirically by Lasareff (1912) via an investigation of two cyanine dyes. Arney *et al.* (1979) addressed this issue of contradicting arguments and conclusions by investigating a number of pigments at oxygen concentration from 0 to 1%. The results indicated the relationship was dependent upon the sample and therefore either scenario might apply to a given colorant.

'Genuine' anoxia closer to 0% oxygen than a few parts per million is practically difficult to achieve with real works of art on paper, some of which include auxiliary paper-based supports while even more are displayed with paper-based mounts: all the paper components tend to desorb oxygen when they are first put into anoxic conditions, thus creating a low oxygen concentration of possibly a few parts per million in a sealed enclosure already filled with inert gas. Continuous oxygen scavenging is the only means of ensuring 'genuine' anoxia, and its continued

effectiveness is difficult to monitor reliably, particularly in the long term. It is easier to carry out experiments to predict the effects of framing with hypoxia achieved by filling with premixed oxygen/inert gas, which can be assumed to increase slightly in oxygen content due to desorption from the paper, but will stay on the 'safe' side of 5% oxygen concentration, from the point of view of any Prussian blue inside the frame.

Any increased colour difference due to the use of modified atmospheres instead of the air normally found within frames were small, generally barely detectable (except in the case of Prussian blue). These results can be considered as justification for the use of anoxic framing for the display of traditional watercolours. They could also have significant impact on the affordability of anoxic frames, as the quality and cost of engineering required in a frame (presently regarded as high) would be reduced if the goal is hypoxia rather than complete, long-term exclusion of oxygen.

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