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A note on the reproductions

The reproductions of complete paintings from the National Gallery's collection in this book have been printed from colour-correct, high-resolution digital scans made with the MARC II Camera. This process was described in 'The MARC II Camera and the Scanning Initiative at the National Gallery', *National Gallery Technical Bulletin*, 23, 2002, pp. 76–82.

Infrared examinations were performed by Rachel Billinge, Rausing Research Associate in the Conservation Department. Infrared reflectography was carried out using a Hamamatsu C2400 camera with an N2606 series infrared vidicon tube. The camera is fitted with a 36mm lens to which a Kodak 87A Wratten filter has been attached to exclude visible light. The infrared reflectogram mosaics were assembled using Vips-ip software.
    For further information about the software see the Vips website at www.vips.ecs.soton.ac.uk

Fading and Colour Change of Prussian Blue: Methods of Manufacture and the Influence of Extenders

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PRUSSIAN BLUE CAN BE DESCRIBED as the first of the modern, totally synthetic pigments, arising only as the result of a deliberate chemical reaction; it has no natural equivalent. Its first preparation in around 1704, by a Berlin colourmaker named Diesbach, appears to have been accidental (the intended product was a cochineal lake),[1] but it is clear that the pigment went into production quite soon afterwards: it was first announced anony-mously in 1710 and the earliest occurrences date from a few years later.[2]

The benefits of an intensely coloured inexpensive blue pigment, flexible in its handling properties and not gritty or difficult to use, were obvious. It could easily be manufactured and its supply was not dependent on the vagaries of transcontinental trade or environmental conditions. The use of Prussian blue spread extremely rapidly, in easel painting,

PLATE 1 Thomas Gainsborough, *Mrs Siddons* (NG 683), 1785. Canvas, 126.4 × 99.7 cm.
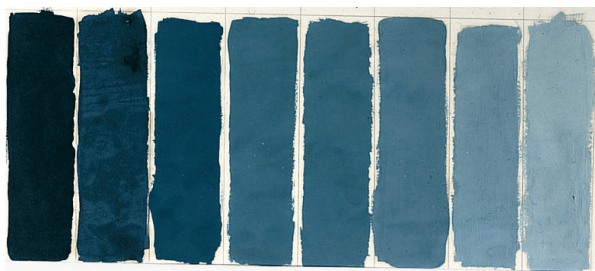
Jo Kirby and David Saunders

PLATE 2 Prussian blue (Aldrich Chemical Company, $Fe^{III}_4[Fe^{II}(CN)_6]_3 \cdot xH_2O$) mixed with lead white in the proportions 1:5, 1:10, 1:20, 1:40, 1:50, 1:100, 1:200 and 1:400 (w/w).

watercolour and for interior decoration and, even though doubts about its permanence were already being expressed by the mid-eighteenth century, its popularity did not diminish: effectively, there were no good alternatives until the syntheses of cobalt blue in 1802 and artificial ultramarine in 1826–7. It is the pigment of cool, white and blue decorative schemes, seen in the feathery touches of Watteau or Gainsborough, the bravura strokes of Tiepolo, or the calm, timeless skies of Canaletto. Mixed with white, its vibrancy of colour surpasses that of the insoluble natural dyestuff indigo, the only other blue pigment available at that time with a similarly high tinting strength. Prussian blue may have a greenish undertone, but this is not always so: the pigment used by Sir Joshua Reynolds for the countess's dress in *Anne, 2nd Countess of Albemarle* (NG 1259, painted in 1760), and by Thomas Gainsborough in *Mrs Siddons* (NG 683, dated 1785;

PLATE 1), is of very good colour. The extraordinarily high tinting strength of Prussian blue is shown in PLATE 2, which illustrates a sample of a modern, high-quality pigment (sample ALP in TABLE 1, pp. 92–3) mixed with different proportions by weight of lead white. Only one part of Prussian blue mixed with 200, or even 400, parts of lead white gives light blue tints very similar to those used for painting skies. FIG. 1 presents reflectance curves for seven of the mixtures illustrated in PLATE 2, showing the characteristic maxima for Prussian blue in the 455 to 475 nm region.

Indigo and Prussian blue have other features in common which would have made the properties of the new pigment relatively familiar to the painter. In oil medium, both need to be ground with a large amount of oil to give a workable paint, and both can be used as glazing pigments as they have a low refractive index. Generally, however, both are used mixed with white as their colour is so deep at full strength that it is almost black. The blue pigment then benefits from the easy handling properties of lead white to allow painterly scumbles and impasto passages to be achieved. Relatively soon after the introduction of the pigment, however, it was suspected that the admixture of so much white had undesirable consequences. Indigo used as an oil paint already had a poor reputation as far as its lightfastness was concerned;[3] when the permanence of Prussian blue also came to be questioned, the presence of white pigment or extender was recognised as a contributory factor.[4]
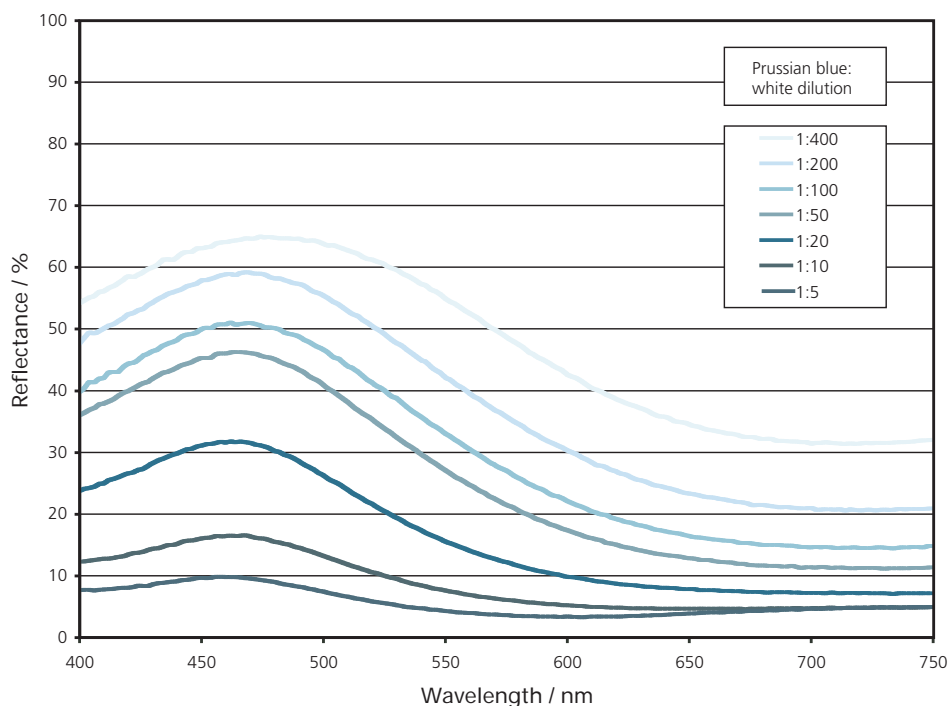

FIG. 1 Reflectance spectra for Prussian blue / lead white mixtures.

Factors that may influence colour change in Prussian blue

An earlier article in the *Technical Bulletin* (1993) gave examples of eighteenth-century paintings in the National Gallery collection in which the fading of Prussian blue had been observed, and discussed eighteenth- and early nineteenth-century reports of the instability of the pigment to light and the factors that might influence this.[5] For convenience these findings are summarised below. The present account describes the experimental investigation of these factors, particularly the method of preparation and the presence of white pigment or extender, based on the examination of samples of late eighteenth- and early nineteenth-century pigments collected from various sources and of pigments prepared in the laboratory.

The original method for preparing Prussian blue, first published in 1724, used dried cattle blood, an alkali derived from the detonation of potassium hydrogen tartrate (potassium hydrogen 2,3-dihydroxybutanedioate) and potassium nitrate, green vitriol (iron(II) sulphate) and alum (in this case, probably the potassium salt, aluminium potassium sulphate). The resulting pale greenish-blue product was treated with hydrochloric acid to give the deep blue pigment.[6] Neither the underlying chemical reaction producing the pigment, nor the nature of the cyano or hexacyanoferrate groups ($-CN$ or $-Fe(CN)_6$) present in the blood, which are essential parts of the complex, was known. The process was therefore very difficult to control. As the chemistry of the preparation became better understood, conditions such as the proportions of the starting reagents, their dilution and the temperature at which the reaction took place could be varied, with the intention of giving a product with a particular colour or range of properties, or of improving the efficiency of the process. By the end of the eighteenth century, many recipes for making the pigment from the essential starting materials of animal matter, an iron salt and alkali (usually potassium-containing) had been published (see TABLE 2, pp. 94–5, for a selection). With increasing knowledge, the procedure could be refined and methods standardised.

Even modern methods of manufacture of Prussian blue are not, however, without problems; the extremely fine particle size and colloidal nature of the pigment make separation of the product from adsorbed water or impurities, including excess starting reagents or contaminants produced during the reaction, particularly hard. These may influence the permanence of the pigment. Differences in working properties and texture depend very much on the treatment of the precipitated particles, which are only 0.01–0.2 μm in diameter and, after the pigment has been washed, tend to agglomerate immediately.[7] Already in the eighteenth century, insufficient washing was known to contribute to hardness of the pigment and other undesirable properties.[8] The tiny, colloidal particles of one variety of potassium-containing Prussian blue are particularly easily dispersed (peptised) in aqueous solutions, giving a blue suspension resembling a solution. This variety is described as 'soluble' and it has long been suspected of being less permanent than other varieties.[9] The lattice structures of the two forms of the pigment ('insoluble' and 'soluble'), with or without alkali metal, discussed below, are slightly different and this factor should also be considered when investigating the permanence. In fact many commercially available varieties of the pigment contain a variable amount of alkali metal, which until after the First World War was most likely to have been potassium. Sodium salts could also have been used, but they tend to give a pigment of inferior colour. After the First World War, the shortage of potassium stimulated the use of ammonium salts in the production of the pigment, and most modern methods for the manufacture of Prussian blue yield the ammonium-containing 'soluble' variety, which has a brighter colour and better alkali resistance.[10]

The deliberate addition of white pigment has been discussed above. The lightfastness of a typical modern Prussian blue pigment has been described as excellent when the proportion of blue pigment is high (90% Prussian blue, 10% titanium white), decreasing as the proportion of white pigment is increased to give very poor durability at 1% blue, 99% white.[11] The white pigment in these experiments is different from the lead white that would have been used in the eighteenth century. By the nineteenth century, zinc white and other whites also became available, all of which have slightly different optical properties (for example, as far as the absorption or reflectance of radiation in the ultraviolet region of the spectrum is concerned),[12] so it is conceivable that they may affect the lightfastness of Prussian blue in different ways.

In addition to admixed white pigment, variable amounts of different inert white extenders may be present. As well as reducing the intensity of colour of the pigment, they also influence other properties such as the softness or ease of grinding; from this point of view their inclusion may be beneficial. The

original method of preparation resulted in the presence of hydrated alumina extender in the pigment, as alum (aluminium potassium sulphate) was one of the ingredients. Alumina may still be added nowadays during the manufacturing process to help the pigment settle, quite apart from its properties as an extender. Other extenders such as starch, calcite or chalk, gypsum and barytes (barium sulphate) could also be used. As with the addition of white pigment, the presence of extenders may influence the light-fastness of the Prussian blue and the addition of white pigment to an already extended blue could increase its impermanence.

From the middle of the eighteenth century onwards it was noted that the change in colour, or fading, of Prussian blue was sometimes reversible. A reversible reduction-oxidation process during which a form of the pigment is produced is the basis of the production of blueprints and cyanotypes.[13] It is also reported that Prussian blues tend to lose their colour on storage in a closed container by a process of reduction, due to the lack of oxygen; this is encouraged by the presence of acidity in the surrounding medium.[14] They also tend to be reduced in the presence of oxidisable media.[15] These changes are reversed when oxygen (from the air, for example) is supplied.[16] The phenomenon has indeed been reported in painted samples of the pigment,[17] but not particularly frequently, and the role of the paint medium has not been investigated previously.

The structure of Prussian blue and the chemistry of its manufacture

Structure

Prussian blue is perhaps the best known of the class of materials described as type II mixed-valence transition metal complexes.[18] It is a hydrated iron(III) hexacyanoferrate(II) complex of variable composition: depending on the method of manufacture and the conditions of precipitation, potassium, sodium or ammonium ions and a variable amount of water may be present. The formula for the alkali metal-free ('insoluble') pigment is $Fe^{III}_4[Fe^{II}(CN)_6]_3 \cdot xH_2O$ (iron(III) hexacyanoferrate(II), where $x = 14-16$). X-ray diffraction and neutron scattering studies have shown that it has a face-centred cubic lattice structure, where the metal sites are occupied by iron(II) and iron(III) alternately, bridged by the cyano groups in a regular array to give a three-dimensional polymeric network. A quarter of the Fe^{II}, C and N sites are vacant. Mössbauer and other spectroscopic

studies have revealed that low-spin iron(II) is co-ordinated octahedrally to the carbon atoms of six cyano groups, while high-spin iron(III) is co-ordinated octahedrally to the nitrogen atoms, and also to the oxygen of co-ordinated water molecules occupying the vacant N sites; the average composition of this mixed environment is $Fe^{III}N_{4.5}O_{1.5}$. For the ideal stoichiometry $Fe^{III}_4[Fe^{II}(CN)_6]_3 \cdot 14H_2O$, a unit cell would, therefore, contain six co-ordinated and eight uncoordinated water molecules, the latter occupying zeolitic-type sites within the cell structure.[19]

The formula for the potassium-containing ('soluble') variety, which has a similar lattice structure, may be written as $KFe^{III}[Fe^{II}(CN)_6] \cdot xH_2O$, where x is variable, but has been reported to be 5 in some syntheses.[20] In this structure, as all the Fe^{II}, C and N sites are occupied, only uncoordinated water can be present. The potassium ion, K^+, acts as a counter ion to complete the neutralisation of the negative charge of the $[Fe^{II}(CN)_6]^{4-}$ group, and potassium ions occupy half the zeolitic-type sites within the unit cell taken up by water in the potassium-free form.[21]

The essential structural element of the pigment framework thus consists of the sequence Fe^{III}–N–C–Fe^{II} and its intense colour arises from an electronic transition (charge transfer transition) between the two valence states of iron: from the Fe^{II} ion to the Fe^{III} ion, which occurs when light in the red region of the visible spectrum, between 690 and 730 nm, depending on the structure, is absorbed.[22]

Chemistry of manufacture

The methods of making Prussian blue fall into two types, direct and indirect. In the direct method, which is a one-step process, a solution of an iron(III) salt, such as ferric chloride, $Fe^{III}Cl_3$, is mixed with a solution of a hexacyanoferrate(II) salt, for example $K_4[Fe^{II}(CN)_6]$. Alternatively, solutions of an iron(II) salt, such as ferrous sulphate, $Fe^{II}SO_4$, and a hexacyanoferrate(III) salt, such as potassium ferricyanide, $K_3[Fe^{III}(CN)_6]$, are mixed. If the iron salts are present in excess, the deep blue precipitate formed is a variety of the so-called 'insoluble' pigment. It was originally thought that the product of the second reaction, which produces a pigment known as Turnbull's blue, was an iron(II) hexacyanoferrate(III), but studies by X-ray diffraction and Mössbauer spectroscopy have shown that both reactions produce iron(III) hexacyanoferrate(II). The molecule contains very little, if any, potassium (although rapid precipitation may cause some to be

brought down as an impurity), but does contain water. If the reagents are mixed in 1:1 molar proportions, or with the hexacyanoferrate in excess, the product is again identical in both cases, being the potassium-containing 'soluble' variety mentioned above, although it may be called 'soluble' Prussian blue or 'soluble' Turnbull's blue depending on the starting materials.[23]
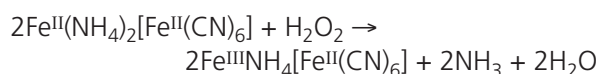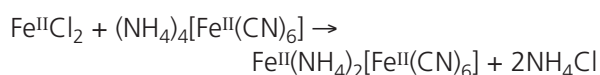
There are thus four direct preparations, producing either 'insoluble' or 'soluble' Prussian blue or Turnbull's blue. The production of 'insoluble' Prussian blue can be summarised as:

$$4Fe^{III}Cl_3 + 3K_4[Fe^{II}(CN)_6] \rightarrow$$
$$Fe^{III}_4[Fe^{II}(CN)_6]_3 + 12KCl$$
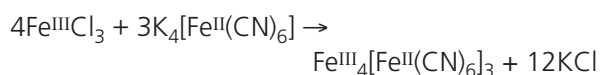
and that for preparing 'soluble' Turnbull's blue as:

$$Fe^{II}Cl_2 + K_3[Fe^{III}(CN)_6] \rightarrow KFe^{III}[Fe^{II}(CN)_6] + 2KCl$$

The indirect method is a two-stage process, based on the reaction between an iron(II) salt and a ferrocyanide salt, typically potassium hexacyanoferrate(II), to give an insoluble white product known as Berlin white (an iron(II) hexacyanoferrate(II), $M_2Fe^{II}[Fe^{II}(CN)_6]$, where M may be ammonium, sodium or potassium, depending on the reagents used). This product is then treated with a powerful oxidising agent such as a chlorate or chromate to give a 'soluble' Prussian blue.[24] The production of Prussian blue from iron(II) chloride and ammonium hexacyanoferrate(II), using hydrogen peroxide as the oxidant, can be summarised as follows:

$$Fe^{II}Cl_2 + (NH_4)_4[Fe^{II}(CN)_6] \rightarrow$$
$$Fe^{II}(NH_4)_2[Fe^{II}(CN)_6] + 2NH_4Cl$$

$$2Fe^{II}(NH_4)_2[Fe^{II}(CN)_6] + H_2O_2 \rightarrow$$
$$2Fe^{III}NH_4[Fe^{II}(CN)_6] + 2NH_3 + 2H_2O$$

The preparation of Prussian blue samples

In order to study the behaviour and characteristics of Prussian blue observed in eighteenth- and nineteenth-century paintings in the National Gallery collection in the context of how the pigment was prepared at the time, it was necessary to have samples of eighteenth- and nineteenth-century pigments for comparison and to study their susceptibility to light. These are listed in TABLE 1 and discussed below. Unfortunately, although a number of early and mid-nineteenth-century samples could be obtained, very few samples from the eighteenth

century were available. The Prussian blue identified in earlier eighteenth-century pictures, such as Gainsborough's *Gainsborough's Forest ('Cornard Wood')* (NG 925) of about 1748, or Canaletto's *Venice: Campo San Vidal and Santa Maria della Carità ('The Stonemason's Yard')* (NG 127), painted between 1726 and 1728 (both discussed in the earlier *Technical Bulletin* article),[25] is likely to have been prepared by some variant of the original method, from cattle blood. However, it was not necessarily the case that any of the collected samples, detailed in TABLE 1, had been so prepared. It was therefore necessary to prepare this type of Prussian blue in the laboratory.

The recipe used to make the pigment from the original ingredients was that published by Robert Dossie in the first volume of his *Handmaid to the Arts* (London 1758). Although the original 1724 recipe, an English version of which Dossie included in the appendix of the second volume, gave an equally fine colour, he says of the 1758 recipe: 'The proportions of the ingredients are more accurately adapted to each other.'[26]

In the original 1724 recipe, four ounces (about 113 g) each of crude tartar (potassium hydrogen tartrate, potassium hydrogen 2, 3-dihydroxybutanedioate) and dried crude nitre (potassium nitrate, KNO_3) were mixed and detonated with charcoal to give an alkali (essentially potassium carbonate, K_2CO_3). This was powdered while still hot, mixed with well-dried, powdered ox blood and heated in a covered crucible until the contents ignited. Subsequently it was heated more intensely until it glowed and there was little further flame. The contents were ground while still hot, added to two pints (about 1.1 litres) of boiling fresh water, boiled and filtered twice. Eight ounces (about 226 g) of crude alum (aluminium potassium sulphate, $AlK(SO_4)_2 \cdot 12H_2O$) were dissolved in two pints of boiling water; this solution was then added to the iron solution and the mixture added rapidly to the hot alkaline blood extract, giving a greenish or blue-green precipitate. The solution was well stirred until effervescence had ceased; the mixture was then left to stand and the precipitate filtered off. On the addition of two or three ounces (about 57–85 ml) of spirits of salt (hydrochloric acid, HCl), the precipitated matter turned blue. It was left overnight, then washed very thoroughly and dried in gentle heat.

According to the recipe, the strength of calcination of the blood and alkali mixture was important as it influenced the resulting colour. In addition, as Dossie pointed out, the use of more alkali gave a

lighter colour, while more acid would, by more efficient removal of the hydrated alumina and other impurities formed during the reaction, give a deeper blue. His modified version (see Dossie 1758 (ii) in TABLE 2) used six pounds (about 2.7 kg) of dried blood to two pounds (about 900 g) of pearl ashes (potassium carbonate), four pounds (about 1.8 kg) of alum and two pounds of green vitriol, not calcined. Four pounds of acid were used to produce the deep blue colour from the greenish precipitate. These proportions and ingredients can be compared with those used in other contemporary recipes in TABLE 2; all claimed to give satisfactory results. Blood was not the only form of animal matter: hoofs, horns and other materials were widely used, sometimes with the addition of extra iron in the recipe. For large-scale preparations, many materials, from rotten wood to chimney soot, were tried for reasons of economy, with varying degrees of success. The emphasis by Carl Hochheimer and others on the need for care in the initial calcination and, if necessary, adjustment of the proportions of ingredients during the preparation is thus entirely understandable. The effects on the final colour were also well understood. In one of Hochheimer's recipes for so-called Paris blue, attributed to the French chemist Philippe Macquer, alum was deliberately omitted, resulting in a very deep blue pigment.[27] By the nineteenth century many contemporary recipes for preparing Prussian blue have as their starting material potassium hexacyanoferrate(II) (*cyano-ferrure de potasse*). However, this was still usually obtained from natural sources. These might include animal matter and iron filings; or perhaps a source of carbon, such as logs or charcoal, with nitrogen from the air and iron filings.[28]

The laboratory preparation based on Dossie's second method was repeated several times, heating the dried blood/alkali mixture in a crucible in a furnace and varying the temperature and heating time. In this preparation the dried blood was a commercial product supplied for use as a garden fertiliser. Several trials were carried out using the 3:1 ratio suggested by Dossie, but better results were obtained by increasing the proportion of dried blood. The best results were achieved by heating 40–50 g of dried blood and 10 g potassium carbonate to about 350°C. The matter burned with an orange flame, producing extremely noxious fumes, and the door of the furnace was periodically opened briefly to allow combustion to continue. The crucible was then removed, the contents stirred and the temperature of the furnace allowed to rise

again; this was continued until no further combustion took place. The temperature was then raised briefly to about 450–500°C, after which the crucible was removed, the contents ground briefly and then added to 300 ml of boiling distilled water. The mixture was boiled for 45 minutes then filtered, giving a clear, usually pale yellow, filtrate.

Iron(II) sulphate (10 g) and aluminium potassium sulphate (20 g) were dissolved separately in distilled water, mixed and then added rapidly to the hot yellow solution, resulting in the immediate production of effervescence, an unpleasant sulphurous smell and a greenish-blue precipitate. Any prolonged delay between the production of the pale yellow dried blood extract and the addition of the alum and iron sulphate solutions tended to result in the formation of brownish iron(III) compounds, spoiling the pigment.

The greenish-blue precipitate was left to settle before filtering, and it was observed that the material became noticeably bluer even on the filter paper. After thorough washing it was treated with hydrochloric acid to remove the hydrated alumina also formed during the reaction, resulting in a fine suspension of slightly purplish Prussian blue. The identity of the pigment was confirmed by Fourier-transform infrared analysis.[29] In one sample (K12a in TABLE 1), the hydrated alumina was allowed to remain as an extender, giving a pale, slightly greenish-blue product.

It is not entirely clear which species are produced by the initial calcination, although the cyano groups in the final Prussian blue must derive from the extract. If a small amount of the filtrate from the calcinations was acidified with 2M sulphuric acid and applied to dipyridyl paper (supplied by Macherey Nagel) a red colour was produced, indicating the presence of iron(II) ions. However, when dried blood is used in the preparation, it seems unlikely that free cyanide and free iron(II) are both present in the filtrate, as in the prevailing alkaline conditions these would react to give Prussian blue prior to the addition of iron(II) sulphate.[30] The second possibility is that the filtrate contains hexacyanoferrate(II), but that the positive dipyridyl test result is due to dissociation of this ion to give free iron(II) in the acidified solution applied to the paper.[31] Finally, both free cyanide and hexacyanoferrate may be present; in alkaline conditions little free iron(II) is present so no Prussian blue will be formed, whereas on acidification for the dipyridyl test free iron(II) is produced, giving the positive result. Certain recipes published by Hochheimer

and Weber (see TABLE 2) use calcined hoofs, a starting material which presumably contained little or no iron, although like others Hochheimer used iron vessels at this stage of the process. Attempts to mimic this method in the laboratory, using collagen-based matter as a starting material, produced no Prussian blue, although a silica rather than iron vessel was used, but this line of investigation was not pursued exhaustively.[32]

The pale colour of the initial product is partly due to the alumina formed on addition of the solution of iron(II) sulphate and aluminium potassium sulphate. However, the main reason for the slow development of the colour is that at least part of the initial product formed by reaction of the iron(II) sulphate and hexacyanoferrate(II) solutions is the 'reduced' form of Prussian blue, Berlin white $K_2Fe^{II}[Fe^{II}(CN)_6]$, which gradually oxidises on contact with air and on acidification of the solution to give 'soluble' Prussian blue $KFe^{III}[Fe^{II}(CN)_6]$.

Although usable quantities of Prussian blue could be obtained by this method, the yields were small compared with the quantities of starting materials. (The small yield was also noted by eighteenth-century writers: see, for example, Hellot 1762 in TABLE 2.) The preparation often failed entirely, particularly if the iron(II) sulphate solution was heated, as recommended by Dossie, before it was added to the filtrate. This gave rise to insoluble iron(III) species (presumably including $Fe^{III}(OH)_3$) which, when added to the filtrate, produced no Prussian blue. It seems likely that although the original recipe was followed as closely as possible, the resulting Prussian blue was probably purer than eighteenth-century commercial products, as great care was taken to wash the precipitate and to dissolve out the alumina (except in the case where this was deliberately retained).

For comparison, modern samples were made by the direct method using either the Prussian blue or Turnbull's blue routes described above, or by the indirect method. In the first preparation by the direct method for Prussian blue, 2.54 g (0.02 moles) of iron(II) chloride, $Fe^{II}Cl_2$, were dissolved in 25 ml of water. Excess hydrogen peroxide was added to convert the iron(II) to iron (III). Separately, 2.84 g (0.01 moles) of ammonium hexacyanoferrate(II), $(NH_4)_4[Fe^{II}(CN)_6]$, were dissolved in 25 ml of water and added slowly to the iron(III)-containing solution with stirring. The blue precipitate that formed was collected, washed with two 50 ml aliquots of distilled water, and dried in a desiccator. This material is labelled SA in TABLE 1. The preparation was

repeated, but the precipitate was washed four times rather than twice, to give sample SB.

Sample SC was also prepared by the direct method for Turnbull's blue, by adding a solution containing 3.29 g (0.01 moles) potassium hexacyanoferrate(III), $K_3[Fe^{III}(CN)_6]$), in 25 ml of water to a solution of 2.54 g (0.02 moles) of iron(II) chloride, $Fe^{II}Cl_2$, in 25 ml of water. The blue precipitate was again washed twice with 50 ml aliquots of distilled water before drying.

Finally, sample SD was prepared by the indirect method. A solution of 2.84 g (0.01 moles) of ammonium hexacyanoferrate(II), $(NH_4)_4[Fe^{II}(CN)_6]$, in 25 ml of water was added to a solution of 2.54 g (0.02 moles) of iron(II) chloride, $Fe^{II}Cl_2$, in 25 ml of water. A pale blue precipitate formed which became dark blue on standing, particularly at the surface where the suspension was in contact with air. An excess of hydrogen peroxide was added to complete the conversion of the first-formed Berlin white to Prussian blue. The precipitate was then washed twice with 50 ml of distilled water and dried in a desiccator.

Description of the eighteenth- and nineteenth-century Prussian blues examined

The particle characteristics and composition of Prussian blues prepared in the laboratory according to an eighteenth-century recipe were compared with those of genuine late eighteenth- and early nineteenth-century samples (TABLE 1), and also with Prussian blues identified in National Gallery paintings (TABLE 3, pp. 96–9). When examined under the optical microscope, the laboratory samples were found to consist of small, irregular fragments of low refractive index, sometimes with the appearance of angular flakes. These were occasionally quite large, flat and plate-like and sometimes a more transparent, paler blue (PLATE 3). Elemental analysis of several of the laboratory-prepared pigments, including K7, K12a and K12b in TABLE 1, revealed the presence of iron and a variable amount of aluminium. Potassium was not detected in these particular samples, but was present in other preparations not included in this table.

Thorough treatment of the pigment with acid would be expected to remove most of the hydrated alumina produced during the preparation. In the case of K7, no aluminium could be detected and rather few translucent angular flakes were present. In practice, however, complete removal of the alumina was not necessarily desired. K12b still contained
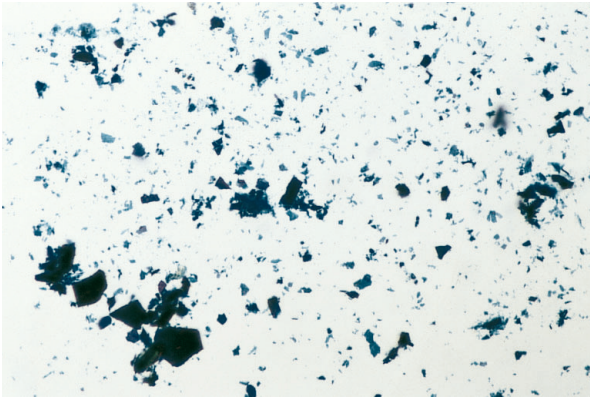
Jo Kirby and David Saunders

PLATE 3 Prussian blue prepared in the laboratory according to an eighteenth-century recipe (sample K12b). Dispersion in odourless kerosene, photographed by reflected light. Original magnification 250×; actual magnification 220×.
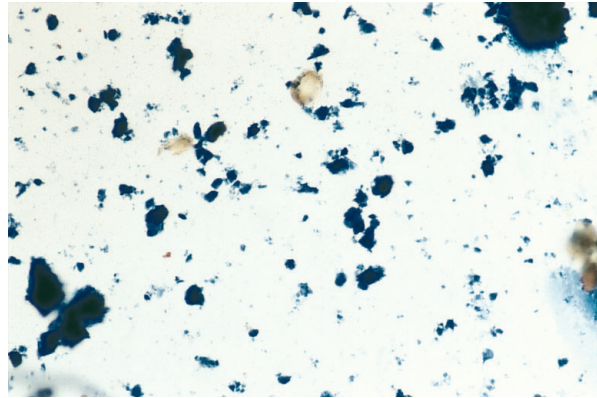

PLATE 5 Prussian blue from Ozias Humphrey's watercolour box (1742–1810), London, Royal Academy. The transparent brownish material is also iron-containing and may have been formed during the preparation of the pigment. Dispersion in odourless kerosene, photographed by transmitted light. Original magnification 250×; actual magnification 220×.
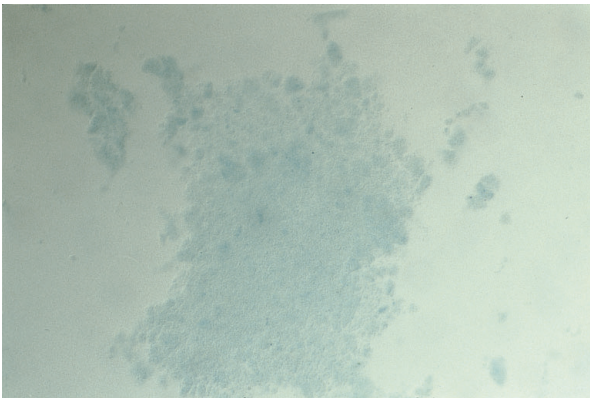

PLATE 4 Prussian blue prepared in the laboratory according to an eighteenth-century recipe, omitting treatment with acid to remove hydrated alumina (sample K12a). Dispersion in odourless kerosene, photographed by reflected light. Original magnification 500×; actual magnification 440×.
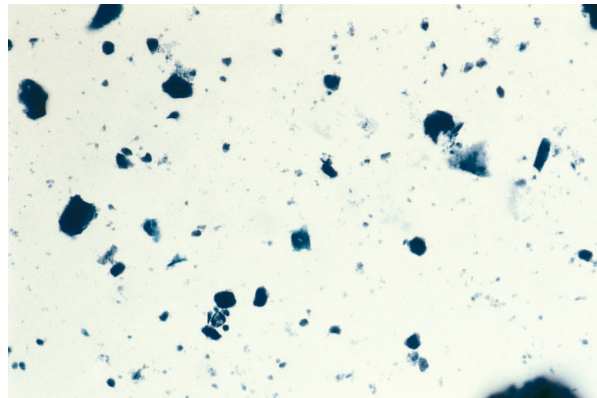

PLATE 6 Prussian blue from Elizabeth Carey's pastel box (1770–1831), London, Victoria and Albert Museum. Dispersion in odourless kerosene, photographed by transmitted light. Original magnification 250×; actual magnification 220×.

some alumina and also a higher proportion of the angular flakes. In K12a, where the alumina had not been dissolved out, the particles were rounded, very translucent and a pale greenish blue, similar to those of a traditional lake pigment (PLATE 4).

In the genuine Prussian blue samples (TABLE 1) and in Prussian blue identified in National Gallery paintings (TABLE 3), analysis revealed the presence of potassium in most cases, along with other elements that derive from the extenders where present. Some of the elements detected by Energy Dispersive X-ray analysis (EDX) may be present because the samples were not washed sufficiently thoroughly to remove unreacted starting materials; for example, chlorine from $Fe^{II}Cl_2$ was detected in samples SA and SB.[33]

The gum was extracted from the paints in water-colour cakes and the oil from those in paint bladders so that the particle characteristics could be examined for all the samples collected. It was found that several pigments resembled the laboratory samples: they showed translucent, paler-coloured, angular flakes, and also contained aluminium. These included watercolour cakes manufactured by Ackermann (AP, AR) and Reeves and Woodyer (MA), powder pigments from the Ozias Humphrey watercolour box and Elizabeth Carey's pastel box (OZ, VB), and the two samples of oil paint from bladders (GA, JSM). PLATES 5 and 6 show typical examples from Ozias Humphrey's watercolour box (OZ) and Elizabeth Carey's pastel box (VB). All date from relatively early in the nineteenth century, or possibly from the late eighteenth century. The
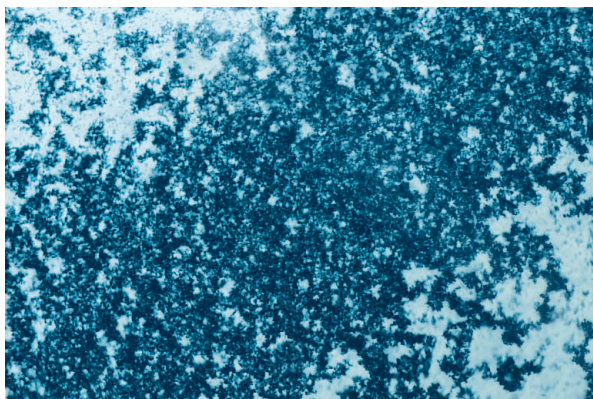
PLATE 7 Modern sample of Prussian blue, supplied by Winsor & Newton, showing rounded agglomerates of pigment. Dispersion in odourless kerosene, photographed by transmitted light. Original magnification 500×; actual magnification 440×.
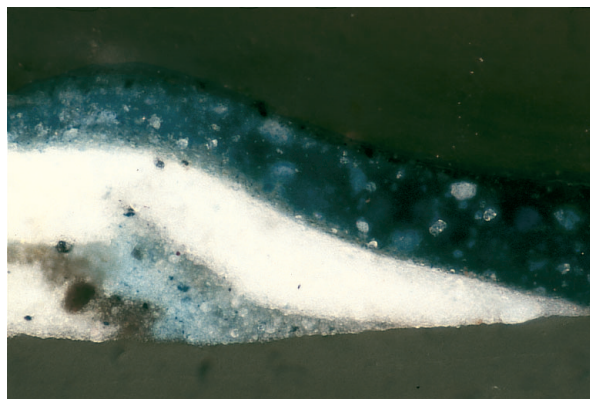

PLATE 8 Gainsborough, *Mrs Siddons*. Cross-section of deep blue stripe on dress. The uppermost dark blue paint layer consists of Prussian blue with a very little white pigment added; this is applied over a layer of lead white. A few characteristic light-coloured flakes of Prussian blue can be seen in the pale blue layer beneath this. Original magnification 500×; actual magnification 440×.

samples from the German pharmacy, which date from 1830 or before, might be expected to share these features (and some of the characteristic angular flakes were observed in samples RB, RC and RE), but the particles tend to coat or to coagulate around the extender, which makes their own features difficult to assess. On the other hand, several samples that probably date from later in the nineteenth century had intensely coloured, rounded agglomerates similar to the modern Winsor & Newton sample (WN, PLATE 7). These included the samples from the Bull paintbox (BCB), the Nicoll samples (NB, NC, NP) and the sample of Turnbull's blue (TB). Deeply coloured clumps of pigment may exhibit bronzing when examined by reflected light. The phenomenon was most obvious in the Winsor & Newton sample and other later pigments, but was also seen in one of the laboratory samples (K7) and an Ackermann sample (AP), suggesting that the method of preparation is not an important factor.

Like the laboratory samples and the earlier pigments described above, Prussian blue identified in eighteenth-century National Gallery paintings often contains angular, flake- or plate-like particles (PLATE 8), which may be a lighter blue. Where instrumental analysis has been carried out, some aluminium has usually been detected. These features appear to be characteristic of the method of preparation in which dried blood or other animal matter and alum are ingredients. The connection between the singular particle shape and the method of preparation has also been observed in an American eighteenth-century interior decoration scheme.[34] The concomitant presence of aluminium

in the particles is a significant feature, however, and it is probable that these qualities, together with the irregularity and variability of the particle morphology, are indicative of the method of preparation. The Prussian blue identified in some early nineteenth-century paintings, such as *A Horse frightened by Lightning* (NG 4927) by Théodore Géricault, shows the same characteristics. Clearly, animal matter continued to be the source of the hexacyanoferrate(II) ion during the early decades of the nineteenth century: Prussian blue with the same features has been identified, for example, in the paintings of J.M.W. Turner.[35]

The alumina incorporated in the pigment as a result of the method of manufacture in effect acts as an extender. Examination of the genuine Prussian blues in TABLE 1 showed that some other sort of extender had often been added. The materials used included starch, calcium salts, barytes, kaolin and, indeed, alumina itself. As mentioned above, alumina may be added during the preparation of the modern pigment to assist precipitation, but the principal reasons for the addition of extender would be to reduce the intensity of the colour and to influence its working properties. Particularly pale varieties of the pigment were sold under names like Antwerp blue; these contained a great deal of translucent extender. One example, a watercolour cake supplied by Ackermann (AA in TABLE 1), is very similar in colour to the laboratory sample in which the hydrated alumina formed was deliberately retained, giving a product similar to a blue lake (K12a). However, the particle characteristics are different: the Antwerp blue does not resemble a 'blue lake', but contains a
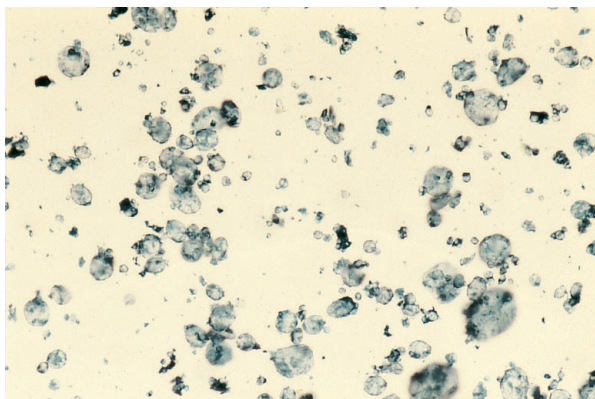
Jo Kirby and David Saunders

PLATE 9 Prussian blue from an old German pharmacy near Darmstadt (1800–30) containing a starch extender, supplied by Professor Dr E.-L. Richter (sample RB). Dispersion in odourless kerosene, photographed by transmitted light. Original magnification 250×; actual magnification 220×.

mixture of dark blue particles, larger colourless particles of extender and only a few pale blue rounded particles, similar to those seen in K12a.

The tinting strength of Prussian blue is so high that it is rarely used undiluted; a relatively large amount of extender could be added by the pigment manufacturer or colourman to improve the properties of the material for decorative or printing purposes, for example, without greatly reducing the strength of the colour. Where the extender has been co-precipitated with the Prussian blue, as for example in the mid-nineteenth-century preparation of *bleu de ciel* and *bleu Marie-Louise*, in which the blue is co-precipitated with barium sulphate, the colour differs from that obtained by grinding barium sulphate with blue pigment.[36] While painting out some of the genuine eighteenth- and nineteenth-century samples for the fading experiments described below it was noticed that, compared with the Winsor & Newton pigment or the pure iron(III) hexacyano-ferrate(II) pigment used as a standard for comparison, some of the samples containing extender were very translucent even at full strength (RD, RE and RF, from the German pharmacy, are examples).

Some of the early nineteenth-century pigments that contain starch grains (RA, RB; PLATE 9) may have been intended for a particular use, or as low-cost pigments. Starch has also been identified in the Prussian blue in several National Gallery paintings: an example is the *Portrait of a Boy* (NG 4034), by an unknown French artist, which is probably early nineteenth century (PLATE 10). The starch grains are clearly visible in the sample from the blue paint illustrated in PLATE 11. While starch-containing pigments

PLATE 10 French School, *Portrait of a Boy* (NG 4034), early nineteenth century. Canvas, 55.9 × 42.5 cm.
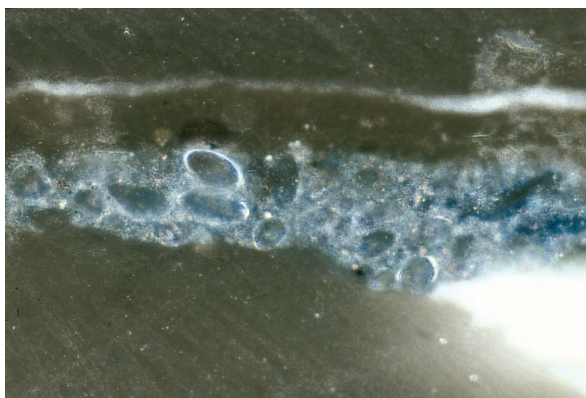
PLATE 11 French School, *Portrait of a Boy* (PLATE 10). Cross-section of dark blue paint of the boy's jacket, showing round or oval translucent starch grains within the blue paint layer. Partial evaporation of the odourless kerosene used to moisten the sample for photography has rendered the grains easily visible. Original magnification 500×; actual magnification 440×.

may not have been in the highest quality range, cost was not necessarily the only factor: the artist may have liked the particular 'feel' of the paint. It was quite noticeable that the extenders present in the eighteenth- and nineteenth-century pigments had a marked effect on their handling properties, both during grinding and when dispersed in the medium. Some extenders gave a particularly pleasant silky feel to the pigment. Constant de Massoul, writing in 1797, noted that Prussian blue was difficult to use in

PLATE 12 Test samples of modern and historic Prussian blues, mixed with different proportions of lead white in oil medium, before (left) and after (right) exposure to light: see TABLE 1 for reference and shade codes. The sequence is identical for the faded panels on the right.

From top (unfaded panels on left, left to right):
row 1: ALP (D, M, L₃–L₁), RE (D, M, L₂), RD (D)
row 2: K12b (L₁, L₃), MC (L₁, L₂), K12a (L₃), RF (D, M, L₂), RD (M)
row 3: K7 (D, M, L₁–L₃), JSM (M, L₂, L₃), RD (L₂)
row 4: K12a (D, M,), GA (M, L₂, L₃), BCB (M, L₁–L₃)

row 5: VB (M, L₂, L₃), MA (L₁, L₃), [blank], AP (M, L₁, L₃)
row 6: JSM (L₂, at 3 different thicknesses), SB (D, M, L₂)
row 7: TB (D, M, L₂), SC (D, M, L₂)
row 8: NB (D, M, L₃), WN (D, M, L₂)
row 9: NP (D, M, L₂)
row 10: NC (D, M, L₂)

watercolour 'because in drying all the particles reunite, even after having been well ground upon Porphyry'.[37] This was found to be so with the laboratory samples prepared from dried blood, and with several others; the presence of any extender improved the grinding markedly.

To offset the greenish undertone of the pigment, recipes for Prussian blue occasionally suggest the addition of red dyestuff, usually cochineal, in some form (see, for example, Cröker 1736 and *Secrets 1790* (v) in TABLE 2). Particles of red lake were observed in the Random and Sneath watercolour cake (RSR in TABLE 1), although insufficient material was available for analysis to be possible. As these red dyestuffs are particularly unstable to light, their fading would be expected to have an effect on the hue of these Prussian blues, quite apart from any sensitivity to light the blue pigment itself might have.

Colour change in samples of Prussian blue

Experimental

To examine the fading of Prussian blue a number of the samples detailed in TABLE 1 were painted out in gum arabic solution as mid-toned watercolour washes on Silversafe paper; these were not particularly pigment-rich, but nor were they characteristic of the very thin washes of Prussian blue sometimes found in watercolours.

As admixture with a white pigment has been implicated in the impermanence of Prussian blue, a set of samples containing different proportions of blue pigment to lead white was prepared in a linseed oil medium. Lead white was chosen because this was the standard white pigment used in the eighteenth and nineteenth centuries. However, as only tiny amounts of some of the genuine eighteenth- and nineteenth-century pigments were available, a preliminary experiment was performed to find appropriate proportions of lead white and Prussian blue. A series of mixtures of pure iron(III) hexacyanoferrate(II), $Fe^{III}_4[Fe^{II}(CN)_6]_3 \cdot xH_2O$ (sample ALP in TABLE 1), with lead white was painted out. The series, seen in PLATE 2, comprises samples with Prussian blue to lead white proportions (weight to weight) of 1:5, 1:10, 1:20, 1:40, 1:50, 1:100, 1:200, 1:400 painted in linseed oil. Three shades, termed *deep* (1:10), *mid* (1:50) and *light* (1:400), were selected and used as visual standards against which to compare mixtures of the Prussian blues with lead white. Some samples were also painted as *very light* or *extremely light* by further diluting the light mixtures with lead white. Because of their scarcity, not all the historic Prussian blues were painted out, and not every shade was prepared for each sample; see TABLE 1 for details. In every case the mixture was ground in cold-pressed linseed oil and painted onto a gessoed panel primed with lead white in linseed oil, PLATE 12. To assess the effect of film depth on

the fading, the very light mixture containing Prussian blue from a paint bladder of 1830–40 (JSM) was painted out at three thicknesses: one, two or three layers.

The samples were all placed in a purpose-built light box at the National Gallery.[38] Briefly, the samples were exposed to light from twelve 65W General Electric *Artificial Daylight* lamps, giving an illuminance at the sample surface of 20–22,000 lux; the temperature and relative humidity during the period of these experiments were 24.5 ±1°C and 36±4% respectively. The light was not filtered to exclude ultraviolet radiation.

The colour of each sample was measured at the outset and periodically during light exposure using a Minolta CR221 colour meter. The standard geometry of this device ensures that the surface to be measured is illuminated at 45° and the light reflected along an axis perpendicular to the surface is measured. This so-called 45/0 geometry ensures that specular reflection (gloss) is excluded from the colour measurement process; the sample area is 3 mm in diameter. The data from the colour meter were converted to Commission Internationale de l'Eclairage (CIE) L*, a*, b* co-ordinates using the standard illuminant D65 as reference.[39] These co-ordinates refer to the lightness (L*), red-greenness (a*), and yellow-blueness (b*) of the sample respectively.

Although dark recovery of colour has been reported for Prussian blue in very thin washes, as found in cyanotypes,[40] the phenomenon is less frequently observed in oil paint films. During the course of the experiments described above, several attempts were made to replicate the recovery of blue colour reported for early samples of Prussian blue when they were stored in the dark after light exposure. Duplicate sets of the samples were placed in the dark after exposure to light for 74 Mlux.h, but the changes in colour that resulted from dark storage were very small. As a result of these experiments, however, three Prussian blues were selected as promising for a further study of this phenomenon. Samples of three Prussian blues, ALP, K7 and SD (see TABLE 1), were painted out on a roughened PTFE plate in linseed oil, a copal varnish dating from 1888, and Liquitex acrylic medium. After initial colour measurement, the plate was exposed in the light box for 6.7 Mlux.h.[41] The colour was measured again and the plate was then placed in a dark metal drawer for two weeks. At the end of the period of dark storage, the plate was measured and exposed to a further 6.7 Mlux.h, then a second period of two weeks in dark storage and, finally, a third exposure of 6.7 Mlux.h.

Results and discussion

All the samples painted out in watercolour faded to some extent on exposure to light, some showing markedly more fading than others. FIG. 2 shows the colour change in two historic samples without extender (MA and TB) and five samples of modern manufacture, one sample of 'insoluble' Prussian blue, $Fe^{III}_4[Fe^{II}(CN)_6]_3 \cdot xH_2O$ (ALP), and four types of 'soluble' Prussian blue, $MFe^{III}[Fe^{II}(CN)_6] \cdot xH_2O$ (where $M = K^+$ for SC and $M = NH_4^+$ for SA, SB and SD). It is clear that the 'insoluble' variety fades much less markedly than the modern 'soluble' samples and the two representative samples of historic pigments, which from their elemental composition (TABLE 1) can be assumed to be 'soluble' Prussian blues.

The effect of extender can be seen by comparing the fading of two samples prepared in the laboratory using Dossie's 1758 recipe (FIG. 3). One half of the material from this preparation (K12) contains undissolved alumina as an extender, while the other portion was treated with acid to remove most of the alumina. The sample containing alumina (K12a) shows a greater colour change. This is at first sight unexpected as the net colour change for complete fading of the paler, alumina-containing sample would be less than that for complete fading of the darker sample. This indicates that the rate of fading of the blue pigment is very greatly increased by the presence of the alumina extender, as has been previously noted.

Although the degree of colour change seems to depend on the type of Prussian blue and is markedly affected by the presence or absence of extender, all the Prussian blue samples showed similar behaviour in terms of colour shift. The pattern is illustrated in FIG. 4: in addition to lightening (which is not shown in this figure) each of the samples becomes less blue (increase in b*) and less green (increase in a*) as it fades.

The samples painted out in oil with lead white show less straightforward behaviour, although the same pattern emerges for many of the samples examined. FIG. 5 shows the colour change for five shades of a mixture of Prussian blue prepared according to Dossie's 1758 recipe (K7) and lead white. In each case, the colour readings for the initial samples have been excluded as there is a large change in the a* and b* co-ordinates during the first 24 hours of light-accelerated ageing. This is due to colour changes in the linseed oil medium that are particularly apparent in the samples containing a higher proportion of lead white.[42] All five shades show a gradual increase in b*, corresponding to a
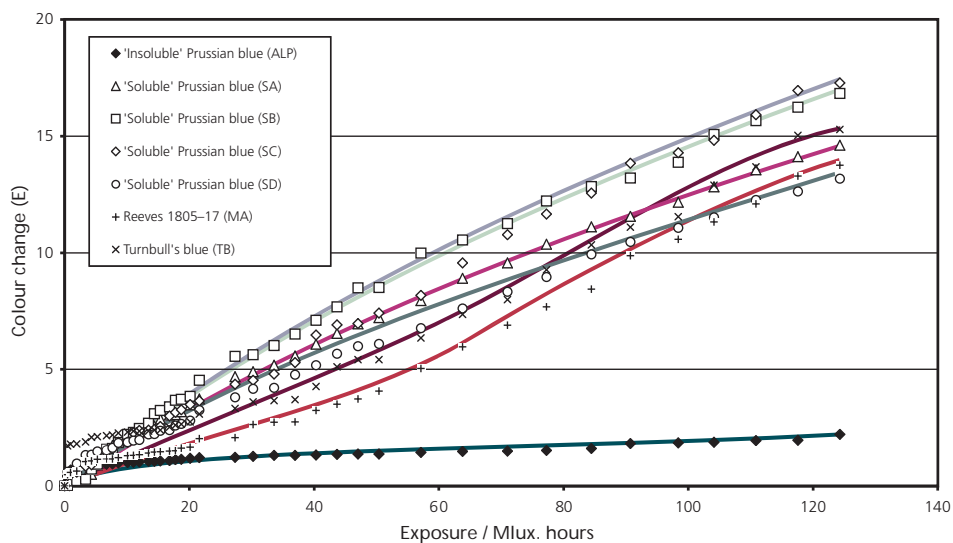
FIG. 2 Colour change (ΔE) for 'insoluble' and 'soluble' Prussian blues in watercolour medium.
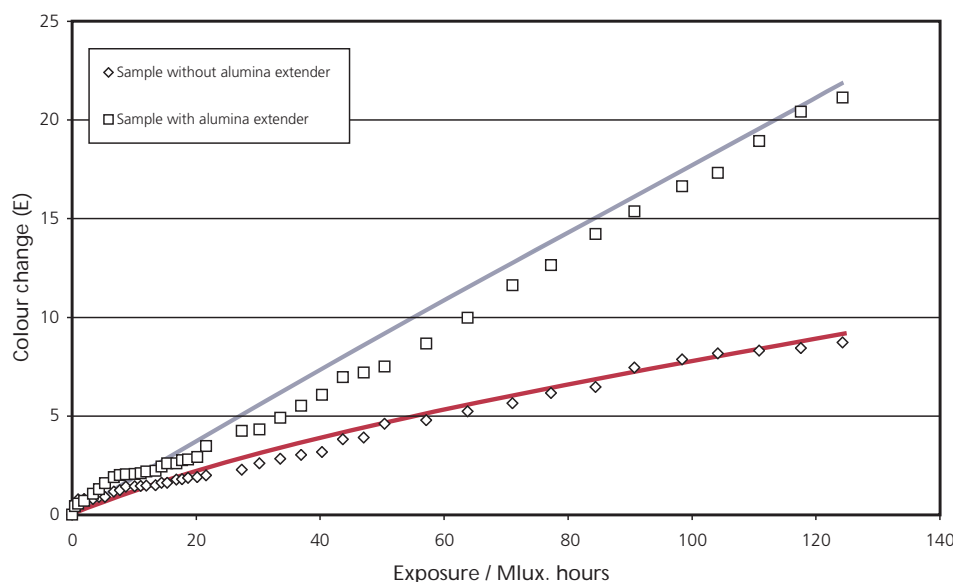

FIG. 3 Effect of extender on colour change (ΔE) in samples of Prussian blue prepared according to Dossie's recipe of 1758 (K12a, with hydrated alumina, and K12b, without) in water-colour medium.

decrease in blueness. The extremely light and very light samples concomitantly decrease in greenness (increase in a*), while the deep sample first increases in greenness before decreasing in greenness. The pattern for the light and mid-toned samples is even more complicated; they first decrease slightly in greenness, then increase in greenness somewhat before consistently decreasing in greenness. This pattern is seen in many of the early Prussian blues examined, for example the sample from Elizabeth Carey's pastel box from the Victoria and Albert Museum (VB) shown in FIG. 6. For all the specimens examined, the extremely light, very light and light samples show an increase in a* of approximately 3 to 7, while the increase in b* is around 14 to 20 (so they are becoming less green and less blue). The final colour is near-neutral on the blue to yellow (b*) axis and appears a pale greenish grey; the

lighter the initial colour the yellower the final grey. The 'sigmoidal' plots for the mid-tones show small overall increases in a* accompanying larger increases of approximately 13 to 20 in b*. The deep tones show smaller changes in both a* and b*, but still sufficient to produce a noticeable loss of blueness.

There are no differences between the behaviour shown by samples of Prussian blue mixed with lead white and samples of extended Prussian blue mixed with less lead white to give the same shade. In other words, the *nature* of the diluent (white pigment or extender) has no effect on the fading of the Prussian blue. This is reinforced by the finding that Prussian blues containing different extenders behave very similarly, for example the sample of Prussian blue prepared from Dossie's 1758 recipe, which is extended with alumina (K12a), and one of the samples from the German pharmacy extended with
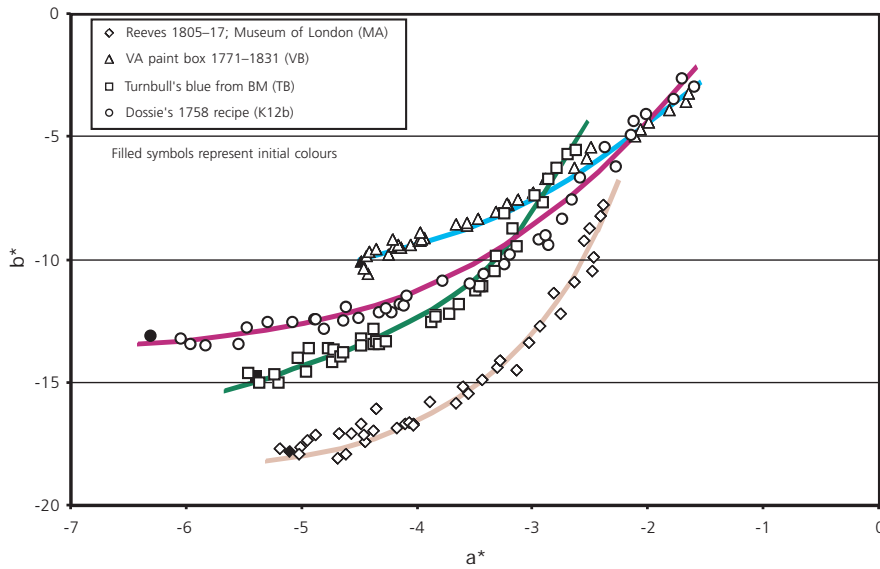
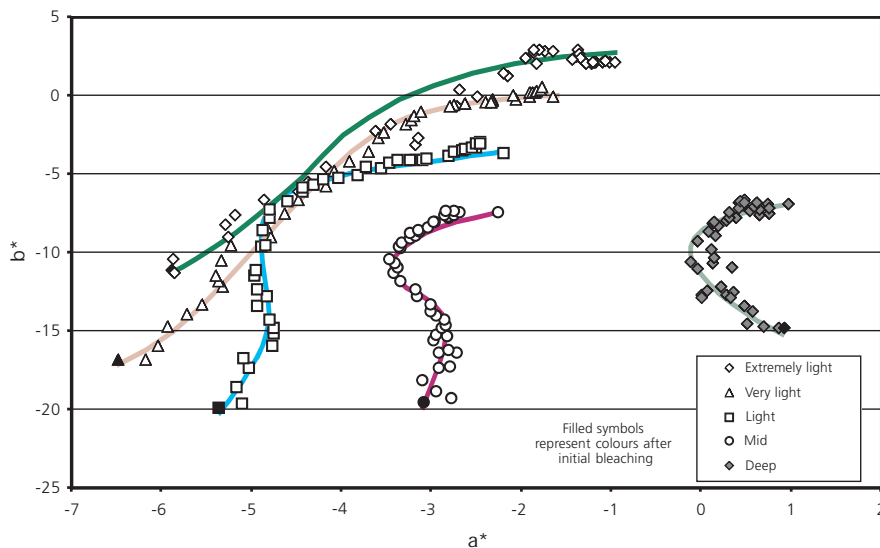FIG. 4 Colour change in four samples of Prussian blue in watercolour medium.

FIG. 5 Colour change for mixtures of Prussian blue prepared according to Dossie's recipe of 1758 (K7) with lead white in oil.

barium sulphate (RE). A trial experiment to investigate the effect of other white pigments, including titanium white, zinc white and barium sulphate, in four different binding media – cold-pressed linseed oil, Liquitex acrylic medium, egg tempera or gum arabic – gave no indication that the nature of the white pigment or the binding medium affected the rate of fading of Prussian blue.

There were no marked differences in the fading of the three test patches comprising a sample of Prussian blue from a paint bladder of 1830–40 (JSM) mixed with lead white and painted out in one, two or three layers. In each case the increase in a* was between 1.1 and 2.1, while the increase in b* (loss of blueness) was between 12.7 and 13.7, indicating that the loss of colour was a surface effect. This confirmed the evidence from cross-sections from paintings and test samples.

As might have been expected, the Random and

Sneath watercolour cake (RSR) that contains a red lake (probably cochineal) showed a noticeable loss in redness on exposure to light, presumably due to fading of the red lake.

The three samples of Prussian blue that were subjected to alternate periods in light and dark showed some small changes in colour. The results are presented in FIG. 7 for the samples in Liquitex acrylic medium. In each case a light exposure of 6.7 Mlux.h resulted in an increase in lightness of 7 to 8 units, a decrease in redness of 4 to 6 units and a decrease in blueness of 3 to 4 units (not shown in the figure). During a period of dark storage some 'recovery' of the colour was observed, again shown (as 'First dark') in FIG. 7. A second period of light exposure produced lightening and loss of redness and blueness comparable to the first light exposure, resulting in colours that were lighter, less red and less blue than those after the initial light exposure.
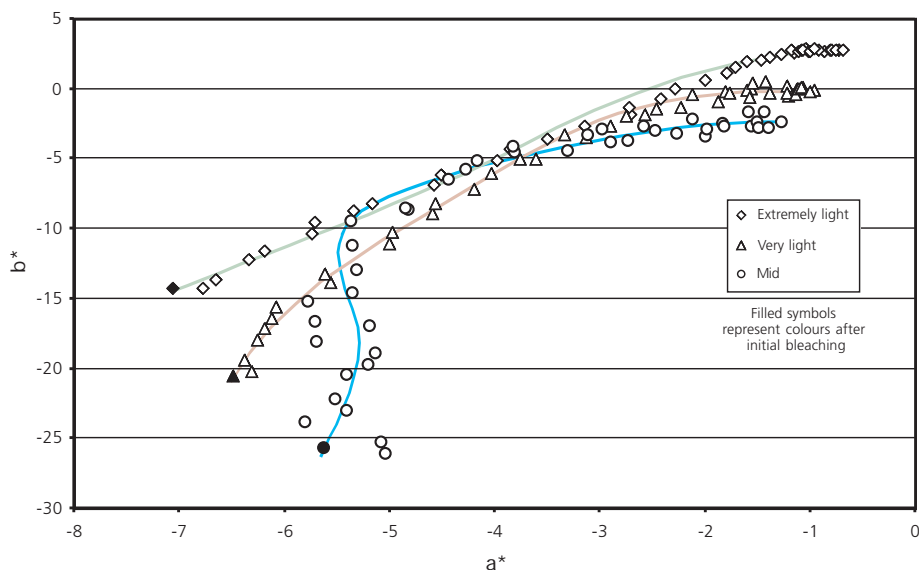
FIG. 6 Colour change for mixtures of Prussian blue from the paintbox held at the Victoria and Albert Museum (VB) with lead white in oil.
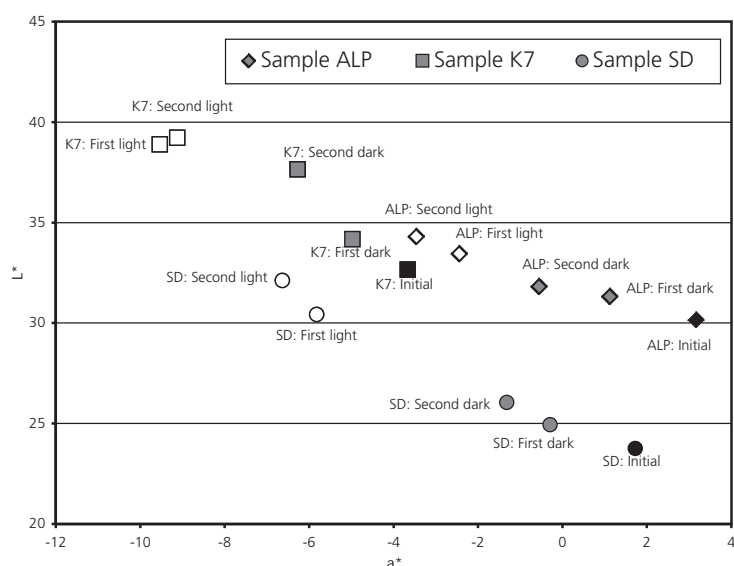

FIG. 7 Colour change accompanying alternating periods of light exposure and dark storage for Prussian blue samples in Liquitex acrylic medium.

Subsequent dark storage caused some recovery, but on each light–dark cycle it is clear that the colour is not fully recovered and that subsequent light exposure causes further irreversible fading.

Conclusions

Factors affecting the degree of fading

The principal factor in the permanence of Prussian blues of different manufactures and dates appears to be the amount of extender present in the supplied pigment. Different methods of preparation only affect permanence in as much as they lead to the incidental introduction of extender, either deliberately or due to inadequate purification of the product. For example, dissolving out the aluminium salt from Prussian blue made from animal blood is easily carried out in a small-scale laboratory experi-

ment, but is less easily achieved in the industrial preparation of the pigment.

Adding white pigment to Prussian blue increases the colour change observed on light exposure. This may be due to increased inter-reflection of light in the paint layer, leading to greater fading, or may simply be a visual effect, because the colour change is more noticeable in the paler blue shades where less Prussian blue is present in the first place. The nature of the white pigment does not seem to affect the fading, nor does it matter whether the white is a deliberate addition to dilute the colour, or a pre-mixed extender added to the Prussian blue by the manufacturer or colourman. When a relatively pure and a much-extended Prussian blue are each mixed with sufficient lead white to produce shades of corresponding lightness, the fading behaviour of the two samples is broadly similar. As alumina extender is present in the light-coloured, translucent, plate-

like flakes characteristic of the eighteenth- and early nineteenth-century pigment, these are particularly likely to exhibit fading, sometimes only at the top of the particle. A small pigment particle surrounded by white pigment in a typical light blue paint film would also be likely to fade.[43] Where the particles form aggregates they are less vulnerable.[44]

Samples in watercolour medium showed similar colour shifts on fading to the mixtures of Prussian blue and lead white in oil medium classified as 'very light' or 'extremely light'. Deeper shades in oil medium showed smaller changes in colour and more complicated colour shifts.

The formula of the pigment has some effect on its permanence; in watercolour, the modern sample of 'insoluble' Prussian blue faded less than modern or historic samples of 'soluble' Prussian blue. However, the counter ion in the different 'soluble' Prussian blues (K^+ or NH_4^+) seems to have little effect on the fading.

The reversibility and chemistry of fading

The films that comprised Prussian blue and white did not regain their colour when placed in the dark after considerable exposure to light, nor did the watercolour samples. The reversible behaviour was only observed in films exposed for relatively short periods before dark storage. It may be that the short-term reversible fading is simply an early stage of the long-term loss of colour, but evidence from other sources seems to indicate that there are two processes involved in the fading of Prussian blue: a fairly rapid, reversible loss of colour, and a slower irreversible colour change. The reversible change can be induced by light in oil paint films, as demonstrated in the experiments described above, but is more usually associated with, and is more dramatic in, thin washes on paper, in cyanotypes for example.[45] The slower irreversible fading is seen in samples in all media and results in a final colour that is best described as yellowish grey.

The chemistry behind these types of colour loss is, however, not completely clear. As already mentioned, the strong blue colour is due to the charge transfer transition between iron(II) and iron(III) in the Fe^{III}–N–C–Fe^{II} moiety. Anything that disrupts this configuration will lead to a loss or shift of colour.

Three reactions of the iron(III) hexacyano-ferrate(II) complex have been implicated in colour change. First, a reduction of Prussian blue to Berlin white, $K_2Fe^{II}[Fe^{II}(CN)_6]$ (also called Everitt's salt),

which can be light-induced, or can be initiated by a reducing agent:

$$Fe^{III}[Fe^{II}(CN)_6]^- + e^- \rightleftharpoons Fe^{II}[Fe^{II}(CN)_6]^{2-}$$
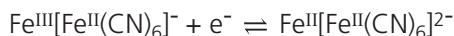
Electrochemical studies of Prussian blue films have shown that the reduction is a single step process and that the blue colour returns on oxidation.[46] Indeed, the $Fe^{II}[Fe^{II}(CN)_6]^{2-}$ complex is an intermediate in the synthesis of Prussian blue from iron(II) and hexa-cyanoferrate(II) ions. As described earlier, mixing solutions containing these two ions yields a pale blue precipitate (containing both $K_2Fe^{II}[Fe^{II}(CN)_6]$ and $KFe^{III}[Fe^{II}(CN)_6]$), which on exposure to air deepens in colour as the Berlin white is slowly oxidised in air, or more rapidly if an oxidising agent is introduced. In the paint film, the situation is not quite the same as in the electrochemical solution studies, where there is a ready supply of counter ions, usually potassium. However, a spectroelectrochemical study of dry films of 'soluble' Prussian blue using *in situ* Fourier transform infrared spectroscopy with atten-uated total reflectance (FTIR/ATR) demonstrated that both reduction and oxidation were possible in the absence of an electrolyte.[47]

This redox process is believed to be responsible for the light–dark bleaching and recovery of cyano-types. Although the paper or size may provide the reducing agent, the fading and recovery has also been noted on cyanotypes printed on glass fibre papers, suggesting that an excess of one of the reagents used in the preparation might act as a reducing agent.[48] In either case, the cycle gradually 'decays' as the reservoir of reducing agent is used up, although if a cyanotype is re-sized further reduc-tion can be induced.[49]

It also seems likely that the reported bleaching of Prussian blue when it is stored in oxygen-free envi-ronments and its recovery on re-exposure to air, for example when the dry pigment is stored in an airtight bottle,[50] results from Prussian blue to Berlin white inter-conversion.

A second possible reaction that would lead to loss of colour in Prussian blue would be the oxida-tion of $[Fe^{II}(CN)_6]^{4-}$ ion. Electrochemical studies of Prussian blue films deposited on electrodes have shown that, unlike the abrupt reduction of Prussian blue to Berlin white, this oxidation proceeds through a number of intermediate steps before yielding a yellowish product, sometimes referred to as Prussian yellow.[51] One intermediate in this reac-tion is the mixed valence compound known as Berlin green. While the oxidation of Prussian blue

to Berlin green is reversible, the subsequent oxidation to Prussian yellow is not fully reversible.[52]

Prussian blue $\rightleftharpoons$ Berlin green

$$[Fe^{II}(CN)_6]^{4-} \rightleftharpoons$$
$$\{[Fe^{III}(CN)_6]_{0.67}[Fe^{II}(CN)_6]_{0.33}\}^{3.33-} + 0.67e^-$$
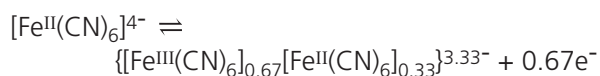
Berlin green $\rightarrow$ Prussian yellow

$$\{[Fe^{III}(CN)_6]_{0.67}[Fe^{II}(CN)_6]_{0.33}\}^{3.33-} \rightarrow$$
$$[Fe^{III}(CN)_6]^{3-} + 0.33e^-$$
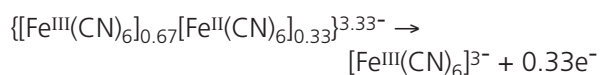
The 'very light' and 'extremely light' paint samples examined in this study all yielded faded products that were a yellowish grey, possibly a mixture of Prussian yellow and a little unreacted Prussian blue highly diluted with lead white.

A third possible reaction of the hexacyanoferrate(II) ion is a substitution reaction. The aquapentacyanoferrate(II) ion is known to be formed by the action of light on Prussian blue:

$$Fe^{III}[Fe^{II}(CN)_6]^- + H_2O \xrightarrow{h\upsilon}$$
$$Fe^{III}[Fe^{II}(CN)_5(H_2O)] + CN^-$$

The reaction is generally studied in aqueous solutions,[53] where there is a ready source of water to co-ordinate at the vacant site on the Fe^{II} ion; in hydrophobic environments, the water molecule co-ordinating to the iron may be one of the unassociated wate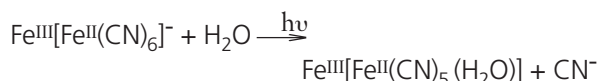r molecules occupying a zeolitic site in the Prussian blue structure. As the aquapentacyanoferrate(II) complex is green, a further reaction must occur during the fading of Prussian blue paint samples examined in this study, as their final colours are considerably less green than the starting materials. It is possible that further substitution reactions displace further cyanide ligands, causing a shift in colour towards yellow and colourless, but this has not been studied in any detail. Alternatively, it is known that $Fe^{III}[Fe^{II}(CN)_5(H_2O)]$ can also undergo redox reactions like those of Prussian blue to yield, for example, the aquapentacyano analogue of Berlin white:[54]

$$Fe^{III}[Fe^{II}(CN)_5(H_2O)] + e^- \rightleftharpoons Fe^{II}[Fe^{II}(CN)_5(H_2O)]^-$$
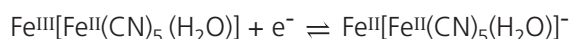
As far as easel paintings are concerned, it seems that if the reversible fading, seen in cyanotypes and watercolour paintings on occasions (or in the absence of oxygen), takes place at all, it is at the very beginning of the deterioration process. The yellowish-grey appearance of changed Prussian blue-containing paint films suggests that the long-term colour changes result from oxidation of the pigment. Perhaps because the appropriate conditions for the regeneration of Prussian blue are not present in the paint film, these changes seem to be irreversible. There is certainly no shortage of oxygen in a drying oil paint film; the oxygen would be consumed both by the oil as it cross links and by Prussian blue as it changes colour. This would accord with eighteenth-century reports of changes in the colour of the pigment relatively soon after painting.[55]

Acknowledgements

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29 Fourier transform infrared analysis was performed by Jennifer Pilc.

30 In the laboratory, an alkaline solution containing free iron(II) and free cyanide ions rapidly produced a dark coloured precipitate containing a mixture of Prussian blue and iron(III) hydroxide.

31 When an alkaline solution of $K_4[Fe^{II}(CN)_6]$ is applied to a dipyridyl paper a positive result is not obtained. However, if the solution is acidified before it is applied to the paper, a positive result is obtained; obviously some Fe^{II} is formed by acid-initiated breakdown of the hexacyanoferrate(II) ion. Indeed, if a solution of $K_4[Fe^{II}(CN)_6]$ is acidified and left for some hours, a 'soluble' Prussian blue is formed, presumably by the reaction of the small amount of free Fe^{II} produced with the remaining hexacyanoferrate(II). No Prussian blue is formed from an alkaline solution of $K_4[Fe^{II}(CN)_6]$.

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41 An exposure of 6.7 Mlux.h is equivalent to around twelve years in a museum under the lighting conditions recommended for oil paintings (200 lux during 56 viewing hours per week), or to exposure outside for one month during typical spring or autumn conditions in London.

42 The initially reversible yellowing and bleaching of a fresh drying oil film, due to conjugation of unsaturated bonds in the oil, is well-known and is particularly apparent in white or light-coloured paint. This effect will be discussed in more detail, from the point of view of colour measurement, in a forthcoming publication.

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TABLE 1 Details of the early Prussian blue samples and pigments prepared in the laboratory

Supplier	Date	Extender[a]	Ref.	Shades in oil[b]
John Nicoll: 'Celestial blue'	mid-19th century	$CaSO_4$: <u>Ca</u>, <u>S</u>, Fe, (K)	NC	LMD
John Nicoll: 'Prussian blue'	mid-19th century	hydrated alumina: <u>Fe</u>, <u>K</u>, Al, (S)	NP	L_2MD
John Nicoll: 'Blue'	mid-19th century	$BaSO_4$: <u>Ba</u>, <u>S</u>, Fe, Si, (Al), (K)	NB	L_2MD
Made from $[(NH_4)_4Fe^{II}(CN)_6]$ + Fe^{III} ($Fe^{II}Cl_2$ + H_2O_2)	–	none: <u>Fe</u>, Cl	SA	–
As SA (above), washed twice with water	–	none: <u>Fe</u>, Cl	SB	L_2MD
Made from $[K_3Fe^{III}(CN)_6]$ + $Fe^{II}Cl_2$	–	none: <u>Fe</u>, K, (Al), (Cl)	SC	L_2MD
Made from $[(NH_4)_4Fe^{II}(CN)_6]$ + $Fe^{II}Cl_2$ + H_2O_2	–	none: <u>Fe</u>, (Al), (S)	SD	–
Aldrich Chemicals (pure $Fe^{III}_4[Fe^{II}(CN)_6]_3$)	n/a	none: <u>Fe</u>, (S)	ALP	L_3L_2LMD
E.-L. Richter: 'Prussian blue, barytes, gypsum'	1800–30	starch[c]: <u>Ba</u>, <u>Ca</u>, Fe, S, (K)	RA	–
E.-L. Richter: 'Prussian blue'	1800–30	starch[c]: <u>Fe</u>, K, S, (Al)	RB	–
E.-L. Richter: 'Prussian blue, gypsum'	1800–30	<u>Fe</u>, K, (Al), (S)	RC	–
E.-L. Richter: 'Prussian blue, kaolin, quartz'	1800–30	<u>Al</u>, <u>Si</u>, K, Fe, (Ti or Ba)	RD	L_2MD
E.-L. Richter: 'Prussian blue, barytes'	1800–30	<u>Al</u>, <u>Ba</u>, <u>Ca</u>, <u>Fe</u>, <u>S</u>, K, Si, (P)	RE	LMD
E.-L. Richter: 'Prussian blue, gypsum'	1800–30	<u>Al</u>, <u>Fe</u>, Ba, Ca, K, S, Si, (Na), (P)	RF	L_2MD
E.-L. Richter: 'Prussian blue, barytes'	1800–30	<u>Ba</u>, <u>Fe</u>, <u>S</u>, K, Si, (Al)	RG	–
A. Burmester: Doerner Institut 'Good Berlin blue from Weimar'[d]	11.4.1855	<u>Al</u>, <u>Fe</u>, K, S, *Si*, (P)	BA	–
A. Burmester: Doerner Institut 'Berlin blue'[d]	30.4.1842	<u>Fe</u>, (Ca), (Cu), (K)	BB	–
The Royal Academy: from Ozias Humphrey's watercolour box	1742–1810	<u>Fe</u>, Al, K, S, (Cu), (Si)	OZ	–
The Royal Academy: Ackermann cake from Reeves box	–	<u>Fe</u>, Al, K	AR	–
The Royal Academy: Random & Sneath cake from Reeves box	–	<u>Al</u>, <u>Ca</u>, <u>K</u>, <u>Fe</u>, S, (Cu), (P)	RSR	–
The Royal Academy: Chinese blue from Bull box	–	<u>Fe</u>, Al, K, *Si*, (S)	BCB	L_3L_2LM
Winsor & Newton alkali ferric ferrocyanide	–	<u>Fe</u>, <u>K</u>, (Al)	WN	L_2MD
Ackermann 'Prussian blue'	1796–1827	<u>Fe</u>, Al, K, (P), (S), (Si)	AP	L_3LM
Ackermann 'Antwerp blue'	1796–1827	<u>Al</u>, <u>K</u>, <u>S</u>, Fe, Si, (K), (P)	AA	–

Supplier	Date	Extender[a]	Ref.	Shades in oil[b]
The Museum of London: Reeves & Woodyer cake	1805–17	Fe, Al, K, (S)	MA	L_3L
The Museum of London: Reeves box cake[e]	18th century	not analysed	MB	–
The Museum of London: Reeves & Inwood powder[e]	1797?	not analysed	MC	L_2L
The Museum of London: Brown of Oxford Street box	1791	not analysed	ME	–
The Victoria & Albert Museum: Elizabeth Carey's box	1770–1831	lead white: Pb, Al, Fe (Cu)	VA	–
The Victoria & Albert Museum: Elizabeth Carey's box	1770–1831	none: Al, Fe, S (K), (Si)	VB	L_3L_2M
Gainsborough's House: paint bladder	early 19th century	Fe, K, (Al), (S), (Si)	GA	L_3L_2M
J.S. Mills: paint bladder	1830–40	Fe, K	JSM	L_3L_2LM
The British Museum: 'Turnbull's blue'	–	Fe, K, (Al), (S)	TB	L_2MD
Made using a recipe of 1758	–	none: Fe, (S)	K7	L_3L_2LMD
Made using a recipe of 1758	–	hydrated alumina: Al, S, Fe	K12a	L_3LM
Made using a recipe of 1758	–	none: Fe, (Al)	K12b	L_3L

Notes

a Determined by EDX analysis. Results indicate the elements detected: strong peaks underlined, minor elements in brackets. In italics = in mounting medium.
b D = deep, M = mid, L = light, L_2 = very light, and L_3 = extremely light.
c Detected by FTIR.
d 'gutes Berliner Blau von Weimar am 11 Apr 1855 … gerieben', 'Berliner Blau vom 30. Apr 1842 …'
e Despite label, pigment is indigo.

Professor Richter's samples are from an old German pharmacy near Darmstadt: E.L. Richter and H. Härlin, 'A Nineteenth-Century Collection of Pigments and Painting Materials', *Studies in Conservation*, 19, 1974, pp. 76–82.

TABLE 2 Ingredients in eighteenth-century Prussian blue recipes and their proportions

Recipe	Animal matter	Alkali	Iron salt	Alum	Notes
Woodward 1724 (the original)	*x* dried blood	4 crude tartar, 4 crude nitre	1 green vitriol, calcined	8	Brown in his experiments on the method found the yield of alkali from the detonation of the tartar and nitre to be 4 parts and the final yield of pigment about 1 part. All solutions hot.
Shaw 1734 (i.e. Woodward)	4 dried blood	4 crude tartar, 4 crude nitre	1 green vitriol, calcined	8	–
Cröker 1736	*x* dried blood	6 tartar, 6 saltpetre	1 English vitriol, calcined (*Englischen Vitriol*)	6	To 1.5 pounds of the blood/alkali mixture add 1.5 *Loth* (3/64 pounds) calcined vitriol. A little cochineal (*Concinelle*) added to the alum solution. No mention of acid.
Dossie's version of the original, 1758	8 dried blood	8 pearl ashes	1 calcined green vitriol	16	Proportion of vitriol is by weight of the calcined material. Greenish precipitate. 6 parts acid to dissolve hydrated alumina, etc. for every 16 parts K_2CO_3 to yield 3 parts product. For a deeper colour (but lower yield) use more acid; for a paler use more alkali.
Dossie 1758 (ii)	3 dried blood	1 pearl ashes	1 green vitriol	2	Green precipitate. 4 parts acid to dissolve hydrated alumina, etc. For a paler colour use, e.g., 3 parts blood and 1 part green vitriol, but then use 5 parts alum.
Hellot 1762 (i)	3 dried blood	3 crude tartar, 3 potash, 1.5 saltpetre	2 (green) vitriol	8	Green precipitate. Sufficient acid. Yield ≤0.375 parts.
Hellot 1762 (ii)	3 dried blood	3 ashes (*cendres gravelées*), 2 crude tartar, 1.5 saltpetre	2 (green) vitriol	8	Washed, dried precipitate will be blue without the need for acid treatment. Yield 2.5 parts, but colour less good.
Hellot 1762 (iii)	3 dried blood	3 quick lime, 2 crude tartar, 1.5 saltpetre	1.5 (green) vitriol	6	Yield *c*.0.4 parts, but of very good colour, 'the effect similar to the most beautiful ultramarine'.
Hellot 1762 (iv)	3 dried blood	3 quick lime, 2 crude tartar, 2 calcined nitre	1 (green) vitriol	4	More product than the preceding, but less fine colour.
Hellot 1762 (v)	3 dried blood	4.5 quick lime, 2 crude tartar, 1.5 saltpetre	1 (green) vitriol	4	Yield *c*.0.5 parts, but the best blue.
Hellot 1762 (vi)	3 dried blood	6 quick lime, 2 crude tartar, 1.5 calcined nitre	1 (green) vitriol	4	Yield *c*.1.6 parts; good colour, similar to (iii).
Le Pileur d'Apligny 1779	8 dried blood	8 potash (*potasse*)	3 iron sulphate (*vitriol de Mars*)	4	Greenish precipitate. 4 parts acid to dissolve alumina and very thorough washing, preferably with hard water.
Secrets 1790 (i)	2 dried blood	2 crude tartar, 2 crude nitre	1 iron sulphate (*vitriol de Mars*)	4	Close to the original method, also included (no. iii). Use more rather than less acid to dissolve hydrated alumina, etc., as colour thereby improved.
Secrets 1790 (v)	2 dried blood	2 crude potash, 1 red tartar, 0.75 oz saltpetre	*x* iron sulphate (*vitriol de Angleterre*)	4	Several other recipes in this book derive from Hellot 1762. Three others include red dyestuffs (cochineal, safflower) to offset the green undertone.
Hochheimer 1792 (ii)	8 dried blood	8 potash	3 iron vitriol	4	Original method also included (no. i). Greenish precipitate; 3–4 parts hydrochloric acid used to dissolve excess alumina, etc.

Recipe	Animal matter	Alkali	Iron salt	Alum	Notes
Hochheimer 1792 (v)	100 animal charcoal	100 potash	25 green vitriol + 6–8 pounds old iron	100	A large-scale preparation starting with 1 *Centner* (100 pounds) burnt horns, hoofs or other animal matter, or even chimney soot; alkaline product called *Blutlauge* whether derived from blood or not. Tests made to adjust proportions of vitriol and alum to get desired shade; addition of acid may be unnecessary.
Hochheimer 1792 (vi)	15 (parts) calcined hoofs (*Klauen-kohlen*)	20 potash	6 English vitriol	40	Method ascribed to Weber (see below); 3 x 25 pound portions of calcined hoofs added to 100 pounds potash at half-hour intervals. Pale blue precipitate treated with acid to obtain a darker blue.
Hochheimer 1792 (vii)	36 (parts) hoofs	16 French tartar, 25 potash	5 English vitriol	16	Described as the Dutch method. 1–1.6 parts sulphuric acid used to dissolve excess hydrated alumina, etc.
Hochheimer 1794 (i)	32–37 (parts) calcined hoofs	50 clean potash	12 green vitriol	80–100	Iron vessel used for calcining the hoofs. Roughly equal proportions of calcined hoofs added to the potash at half-hour intervals. Treat with acid if required. In a modification of this method, for every 2 parts potash used, 1 part acid and 4 parts alum solution are added to the alkaline solution; sufficient vitriol is then used to complete the reaction.
Weber 1793 (i)	20 (parts) calcined hoofs	18 raw potash	5 or 6 (green) vitriol	8 or 10	The alkaline solution should be greenish: absence of colour a bad sign. 0.75 parts sulphuric acid added to alum/iron sulphate mixture before addition to alkaline extract; another 3 parts iron salt added subsequently to ensure completion of reaction.
Weber 1793 (ii)	14 (parts) calcined hoofs	13 pure potash	5 (green) vitriol	15	Or use 20 parts alum, then use acid to redissolve the excess precipitated as hydrated alumina.
Massoul 1797	2 dried blood	1 tartar alkali	1 iron sulphate (Martial vitriol)	3	Yellowish-green alkaline solution. On the addition of the alum/iron sulphate the mixture becomes reddish brown, with a sediment that is blue on the surface, yellow in the centre. It turns green, then blue on exposure to the air. Acid optional.

Sources

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Notes

Alum: aluminium potassium sulphate, $AlK(SO_4)_2 \cdot 12H_2O$

Green vitriol: iron(II) sulphate, $FeSO_4 \cdot 7H_2O$

Tartar: potassium hydrogen tartrate, the mono potassium salt of (+)-2,3-dihydroxybutanedioic acid. Tartar alkali is potassium carbonate

Nitre, saltpetre: potassium nitrate, KNO_3

Pearl ashes, ashes, *cendres gravelées*: potassium carbonate, K_2CO_3

Potash, potasse: unclear whether this is potassium hydroxide, KOH, or potassium carbonate

Quick lime: calcium oxide, CaO

The acid used was usually hydrochloric acid, HCl, spirits of salt.

TABLE 3 Examples of occurrences of Prussian blue in National Gallery paintings

British School[1]

Artist	Painting	Date	Occurrence of pigment	Elements detected	Notes
Thomas Gainsborough	*Gainsborough's Forest* ('*Cornard Wood*'), NG 925	*c*.1748	sky (trace)	–	Pale, flake-like particles; faded
	Portrait of the Artist with his Wife and Daughter, NG 6547	*c*.1748	wife's dress; sky (trace)	Fe, Al	Flake-like particles
	Mr and Mrs Andrews, NG 6301	*c*.1748–9	dress; sky (trace)	–	Transparent, flake-like particles; possibly faded
	John Plampin, NG 5984	*c*.1755	sky (with other pigments)	Al, Fe, K, (Ca) (Si)	Flake-like particles; faded
	The Painter's Daughters chasing a Butterfly, NG 1811	probably *c*.1756	skirt of left-hand girl	–	Some large, greenish-blue flakes; faded
	Dr Ralph Schomberg, NG 684[2]	*c*.1770	sky	–	Calcite ($CaCO_3$) present in Prussian blue-containing paint, but unclear if as extender for blue pigment or deliberate addition to paint
	The Watering Place, NG 109	*c*.1774–7	sky	–	Flake-like particles; faded
	Mrs Siddons, NG 683	*c*.1783–5	dress	–	Some flake-like particles
	Mr and Mrs William Hallett ('*The Morning Walk*'), NG 6209	*c*.1785	dress (with lead white, black)	Si, Fe, K, (Mg)	–
William Hogarth	*The Graham Children*, NG 4756	1742	older girl's dress (with ultramarine)	–	–
	Marriage à la Mode, NG 113–118[3]	before 1743	various contexts	–	–
Sir Joshua Reynolds	*Anne, Countess of Albemarle*, NG 1259	probably 1759–60	dress	Fe	Some flake-like particles
	Colonel Banastre Tarleton, NG 5985	1782	coat	–	–
George Stubbs	*The Millbanke and Melbourne Families*, NG 6429	*c*.1769	clothing; sky; foliage	–	–

Dutch School

Artist	Painting	Date	Occurrence of pigment	Elements detected	Notes
Jan van Huysum	*Flowers in a Terracotta Vase*, NG 796[4]	1736	various	–	–
Jan van Os	*Fruit and Flowers in a Terracotta Vase*, NG 6520[5]	1777–8	various	–	–

French School

Artist	Painting	Date	Occurrence of pigment	Elements detected	Notes
Nicolas-Toussaint Charlet	*Children at a Church Door*, NG 4140	*c.*1817–45	sky	–	Starch extender (also present in black paint)
Imitator of Thomas Couture	*Caught by the Tide*, NG 4613	1860–90	dress	Fe, Si, (Al)	Amorphous, stain-like appearance; quartz extender
Jacques-Louis David	*Portrait of Jacobus Blauw*, NG 6495	1795	coat	–	–
	Portrait of the Vicomtesse Vilain XIIII and her Daughter, NG 6545	1816	dress	–	–
Hilaire-Germain-Edgar Degas	*Princess Pauline de Metternich*, NG 3337	*c.*1865	underlayers	Fe	Finely divided
	Hélène Rouart in her Father's Study, NG 6469	*c.*1886	dress	–	–
Ferdinand-Victor Eugène Delacroix	*Ovid among the Scythians*, NG 6262	1859	sky	Fe, Al, K	Finely divided
Jean-François Detroy	*Time unveiling Truth*, NG 6454	1733	sky; drapery	–	Some flake-like particles
	Jason swearing Eternal Affection to Medea, NG 6330	1742–3	drapery	–	–
	The Capture of the Golden Fleece, NG 6512	1742–3	sky; drapery	–	–
François-Hubert Drouais	*Le Comte de Vaudreuil*, NG 4253	1758	coat	<u>Al</u>, Si, Ca, Fe K	A deep, stain-like blue as very little white present
French School	*Portrait of a Boy*, NG 4034	before 1810	jacket	Fe, Al, K, Ca	Starch extender
French School	*Portrait of a Lady*, NG 2218	19th century	background	<u>Si</u>, <u>Al</u>, Fe, K	Silica-containing extender (kaolin type?)
Jean-Louis-André-Théodore Géricault	*A Horse frightened by Lightning*, NG 4927	*c.*1813–14	greenish horizon	<u>Al</u>, Fe, (K), (Si), (Ca)	Large flake-like particles
Jean-Baptiste Greuze	*A Child with an Apple*, NG 1020	late 18th century	cushion	–	–
Nicolas Lancret	*The Four Times of Day: Afternoon*, NG 5869	1739–41	sky	<u>Al</u>, Fe, K	Some large, translucent flake-like particles
Edouard Manet	*Music in the Tuileries Gardens*, NG 3260[6]	1862	sky underpaint	–	Very finely divided
Claude-Oscar Monet	*Bathers at La Grenouillère*, NG 6456[7]	1869	sky; clothing	–	–
Adolphe Monticelli	*A Vase of Wild Flowers*, NG 5015	Probably 1870–80	various	Fe, K	–
	Still Life: Oysters, Fish, NG 5013	*c.*1878–82	various	Fe	–
	Still Life: Fruit, NG 5014	*c.*1878–82	various	<u>Ca</u>, <u>S</u>, Fe, K, Al, Si	Calcium sulphate extender
Adolphe Monticelli (after?)	*Torchlight Procession*, NG 5009	probably 1870–86	various	<u>Ca</u>, Fe, K (Si)	Calcite (CaCO$_3$) extender; notably bright colour
Jean-Baptiste Perronneau	*A Girl with a Kitten*, NG 3588	1745	background; dress	–	Pastel on paper; pigment mixed with varying amounts of chalk to give different shades of blue

TABLE 3 Examples of occurrences of Prussian blue in National Gallery paintings (continued)

Italian School

Artist	Painting	Date	Occurrence of pigment	Elements detected	Notes
Attributed to Bernardo Bellotto	*Venice: Upper Reaches of the Grand Canal facing Santa Croce*, NG 2514	after 1768	sky	–	Some fading
Canaletto	*Venice: Campo S. Vidal and Santa Maria della Carità ('The Stonemason's Yard')*, NG 127[8]	1726–30	sky	–	Flake-like particles
	Venice: The Feast Day of Saint Roch, NG 937[9]	*c.*1735	sky; draperies	<u>Ca</u>, Fe, Al	Flake-like particles (possibly calcite or chalk present)
	Venice: A Regatta on the Grand Canal, NG 938	*c.*1735	sky; water; draperies	–	–
	Venice: The Upper Reaches of the Grand Canal with S. Simeone Piccolo, NG 163[10]	*c.*1738	sky; water	–	Flake-like particles; some fading
	Venice: The Basin of San Marco on Ascension Day, NG 4453	*c.*1740	sky; water	–	–
	A Regatta on the Grand Canal, NG 4454	*c.*1740	sky; water	–	Flake-like particles
	Eton College, NG 942	*c.*1754	sky; water	–	–
Studio of Canaletto	*Venice: Palazzo Grimani*, NG 941	*c.*1756–68	sky	–	Faded
Corrado Giaquinto	*Apotheosis of the Spanish(?) Monarchy(?)*, NG 6229	*c.*1751	sky	Fe, (Al)	–
Francesco Guardi	*Venice: The Punta della Dogana*, NG 6156	1780s	sky	–	–
	Venice: The Giudecca with the Zitelle, NG 6157	1780s	sky	–	–
Italian School	*Portrait of a Woman*, NG 2217	19th century	sky	<u>Al</u>, Fe, K	–
Giovanni Battista Tiepolo	*Saints Maximus and Oswald(?)*, NG 1192	*c.*1745	sky	–	–
	An Allegory with Venus and Time, NG 6387[11]	*c.*1754–8	sky; drapery	–	Flake-like particles

Spanish School

Artist	Painting	Date	Occurrence of pigment	Elements detected	Notes
Francisco de Goya	*A Picnic*, NG 1471	1785–90	sky; foliage	Fe, Al	With ultramarine
	Doña Isabel de Porcel, NG 1473[12]	before 1805	in clothing of overpainted male portrait beneath	–	Painted over a portrait of a man in uniform
	The Duke of Wellington, NG 6322	1812–14	in sitter's decorations	–	–

Prussian blue in retouchings and overpaint

Artist	Painting	Date	Occurrence of pigment	Elements detected	Notes
Follower of Botticelli	*Saint Francis*, NG 598	1490–1500; retouching, probably 19th century	angel's robe	–	Starch extender
Master of the Mornauer Portrait	*Portrait of Alexander Mornauer*, NG 6532[13]	*c.*1464–88; 18th-century overpaint	blue overpaint over panelled background	Fe, Al	Flake-like particles
Pietro Perugino	*The Virgin and Child with an Angel*, NG 288.1	*c.*1496–1500; later retouchings	extensive use on false additions	–	–

Notes

Note: Usually the Prussian blue has been mixed with variable amounts of lead white (thus lead is always detected, but is omitted here); other pigments may also be present. Where elemental analysis was not carried out the pigment was identified microchemically (it reacts rapidly with alkali, giving a brown product), or by FTIR. Prussian blue is also often found in mixtures to make greens.

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2   D. Bomford, A. Roy and D. Saunders, 'Gainsborough's "Dr Ralph Schomberg"', *National Gallery Technical Bulletin*, 12, 1988, pp. 44–57, esp. pp. 49–50.
3   D. Bomford and A. Roy, 'Hogarth's "Marriage à la Mode"', *National Gallery Technical Bulletin*, 6, 1982, pp. 44–67, esp. pp. 62–4.
4   J. Kirby and D. Saunders, 'Sixteenth- to eighteenth-century green colours in landscape and flower paintings: composition and deterioration', *Painting Techniques: History, Materials and Studio Practice; Contributions to the Dublin IIC Congress, 7–11 September 1998*, eds A. Roy and P. Smith, London 1998, pp. 155–9, esp. pp. 155–6.
5   Kirby and Saunders 1998 (cited in note 4).
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9   D. Bomford and A. Roy, 'Canaletto's "Venice: The Feastday of S. Roch"', *National Gallery Technical Bulletin*, 6, 1982, pp. 40–3.
10 Bomford and Roy 1993 (cited in note 8).
11 J. Kirby, 'Fading and Colour Change of Prussian Blue: Occurrences and Early Reports', *National Gallery Technical Bulletin*, 14, 1993, pp. 62–71, esp. pp. 62, 64.
12 M. Wyld, 'Goya's Re-use of a Canvas for "Doña Isabel"', *National Gallery Technical Bulletin*, 5, 1981, pp. 38–43.
13 S. Foister, 'The Portrait of Alexander Mornauer', *The Burlington Magazine*, CXXXIII, September 1991, pp. 613–18.