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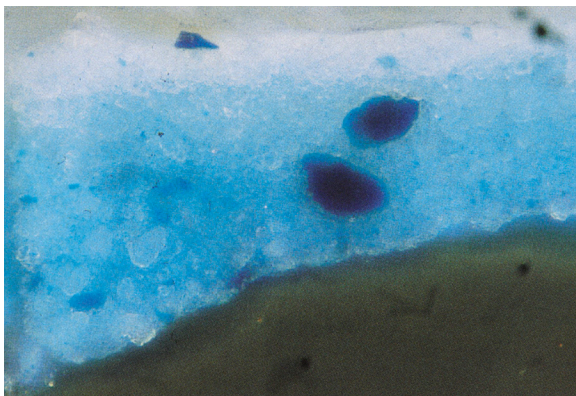
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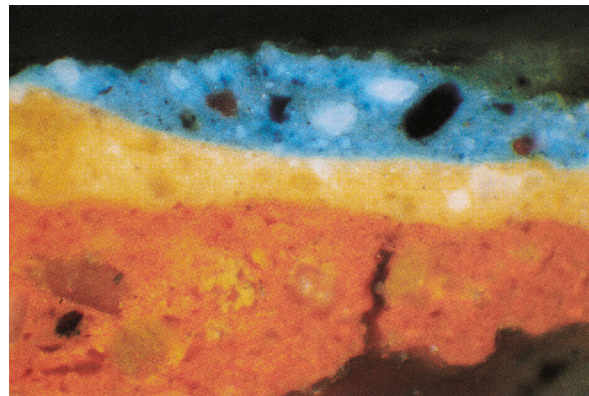
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**Plate 1** Giovanni Battista Tiepolo, *An Allegory with Venus and Time* (NG 6387), c.1754. Canvas, 292 x 190.4 cm. Detail of Time's blue drapery.



**Plate 2** Palest tint of drapery, showing fading at the top of the paint layer, which contains a little Prussian blue with lead white. (Lower layers missing.)



**Plate 3** Darker tone of drapery, unfaded.

1. Prussian blue with lead white.
2. Yellow undermodelling layer: yellow ochre and a little lead white. (This layer is not present in every sample and varies in colour in different areas of the picture.)
3. Reddish-brown ground: red ochre with red lead.

Plates 2 and 3 are photomicrographs of paint cross-sections photographed under the microscope by reflected light at 750x and 250x respectively. Actual magnification on the printed page 600x and 220x.

# Fading and Colour Change of Prussian Blue: Occurrences and Early Reports

*Jo Kirby*

If one considers the palette of the mid-seventeenth-century painter, it is not immediately obvious that there was any shortage of blue pigments: the vivid, almost overpowering splendour of ultramarine and the sparkling greener blue of azurite come immediately to mind. Smalt, at its best and when freshly painted, could have a surprising intensity of colour.

In practice, however, all these pigments had their disadvantages: there was no one perfect blue. Ultramarine was scarce, extremely dear and, partly because of its pronounced purplish hue, did not necessarily mix well with other colours. By the latter part of the seventeenth century azurite had also become extremely scarce: indeed, it appears to have fallen into disuse in the eighteenth century. Its synthetic equivalent, blue verditer, seems always to have found greater favour as a decorator's colour; a somewhat gritty texture and greenish cast, which tended to become more pronounced with the passage of time, made it less popular with painters in oil and watercolour. Smalt was very pale when ground at all finely and it sank in oil. It also gradually lost its colour in an oil medium, which itself discoloured badly.<sup>1</sup> All these blues were transparent: their intensity of colour depended upon their being coarsely ground. Indigo, the only organic blue pigment then used in oil, had a deep, intense colour and, mixed with yellow, was useful for making greens, but it was known to fade and was not regarded highly. Thus, by the beginning of the eighteenth century, the choice of blue pigments was in fact very restricted.<sup>2</sup>

Then, in 1710, an announcement for a new blue pigment appeared in *Miscellanea Berolinensia*.<sup>3</sup> Invented in Berlin several years previously, and subsequently known as Prussian blue, the pigment was described as durable in both oil and watercolour; resistant to acids; unchanged by atmospheric conditions; easily ground to the finest powder and with excellent covering power. It was also non-poisonous, mixed well with other colours and, the notice claimed, 'it survives in quick lime.' Not the least of its virtues was that its price was one-tenth that of the

dearest ultramarine, with which it was compared very favourably a few years later: 'Nowadays a very beautiful blue pigment has been invented in Berlin, equal to or excelling Ultramarine ...'<sup>4</sup>

Not surprisingly, the earliest reports of the use of Prussian blue appear in the neighbourhood of Berlin. Traces of Prussian blue and lead white, applied over gold leaf, were detected on one of the original lead appliquéés on the *Ehrengitter* (decorated fencing) at Charlottenburg Castle, Berlin.<sup>5</sup> The lead appliqué sampled dates from 1712. Use of the pigment spread remarkably quickly, however: it appears to have been available in France and in England well before the method of manufacture was first published by John Woodward in 1724, in London.<sup>6</sup> Its presence has, for example, been confirmed in a number of paintings by Watteau, who died in 1721. In his haunting picture of a clown, *Gilles* (Paris, Musée du Louvre), painted in Paris and probably dating from around 1718–19, it is found mixed with lead white in the blue paint of the sky.<sup>7</sup> It has also been found in *Récréation italienne* (Berlin, Charlottenburg Castle), which may date from around 1715–16,<sup>8</sup> and in the *Comédiens italiens* (Washington, National Gallery of Art), which was probably painted during Watteau's stay in London, 1719–20.<sup>9</sup>

## Occurrences of faded Prussian blue

The modern artists' pigment is generally held to be reasonably light-fast under normal conditions; suppliers of artists' materials describe it as being durable or moderately durable in oil and in watercolour, unless used in an extremely thin wash or mixed with a very high proportion of white.<sup>10</sup> A thin wash of the pigment is said to fade in strong light, but regain its colour in the dark.<sup>11</sup> In mixtures with white, the light-fastness of the pigment is described as excellent when the proportion of blue is high (90% Prussian blue, 10% titanium white), but decreases as the proportion of white pigment is increased; a mixture of 1% Prussian blue to 99% titanium white shows poor durability.<sup>12</sup>

During a recent examination of Gainsborough's early landscape, *Gainsborough's Forest* ('Cornard Wood') (NG 925), of c.1748,<sup>13</sup> it was noticed that the palest tint of the sky had faded in comparison with the identical paint on the turnover edge, which had been protected by the frame. Samples of paint taken from different areas of the painting revealed that where the sky paint had been protected by another paint layer — where the foliage of a tree had been painted over the sky, for instance — it was found to be a brighter blue than that of the exposed sky paint. Analysis showed that the sky had been painted using a little Prussian blue mixed with a great deal of lead white. In the cross-section prepared from the faded paint, this layer appeared greyish white in colour, with very little blue visible except for a few specks at the bottom where it had been protected to some extent by the paint above.

The same phenomenon was observed in Gainsborough's *Mr and Mrs Andrews* (NG 6301) of c.1750 and *The Watering Place* (NG 109) of c.1777, where faded Prussian blue was found in the sky paint, mixed with lead white. In *Mrs Siddons* (NG 683), which Gainsborough completed early in 1785, the dark blue stripes of the sitter's dress, which contained a high proportion of Prussian blue, appeared unchanged, but the light blue, painted in Prussian blue mixed with a high proportion of lead white, had faded. The same mixture of pigments was found in the sky of two paintings by Richard Wilson: *Holt Bridge on the River Dee* (NG 6196) and its companion *The Valley of the Dee* (NG 6197); as before, the blue had faded.<sup>14</sup> When Watteau's *Récréation italienne* was examined in 1985 at the Institut für Technologie der Malerei, Staatliche Akademie der Bildenden Künste, Stuttgart, the Prussian blue used in the paint of the sky was similarly found to have faded, except in those areas covered by the frame.

The presence of faded Prussian blue has also been observed in a number of Italian School paintings in the Collection. In Canaletto's *Venice: Campo San Vidal and Santa Maria della Carità* ('The Stonemason's Yard') (NG 127), painted between 1726 and 1728, faded Prussian blue can be found, mixed with lead white, in the light blue paint of the sky. The same effect was observed in *Venice: Upper Reaches of the Grand Canal with San Simeone Piccolo* (NG 163), dating from c.1738, in *Venice: The Basin of San Marco on Ascension Day* (NG 4453), probably dating from c.1740, and in *Venice: The Feast Day of Saint Roch* (NG 937), of c.1735, where it is less marked.<sup>15</sup>

On the surface of the painting the pale blue areas — typically skies, as the above examples show — where fading has occurred often have a patchy, greyish appearance. The phenomenon is easier to see in

cross-sections of paint and can be illustrated by a sample taken from the lightest area of Time's blue drapery in Tiepolo's *An Allegory with Venus and Time* (NG 6387) (Plates 1 and 2, p. 62), perhaps dated c.1754.<sup>16</sup> The fading is most obvious at the top of the layer, which consists (as in all the examples described) of lead white mixed with a little Prussian blue. The colour changes gradually from a greyish white at the top, hardly recognisable as blue apart from the larger, more intensely coloured, translucent flakes and undispersed lumps of blue pigment, to a more intense blue at the bottom of the layer. Very occasionally, although not in this case, it is possible to see flakes of blue within the faded part of the layer which have become greenish at the top. In a cross-section prepared from a paint sample taken from a brighter blue area of the same drapery, however, it can be seen that the uppermost layer of blue paint contains a far higher proportion of Prussian blue mixed with lead white and appears unchanged (see Plate 3).

Where the presence of Prussian blue is suspected it is important that it be confirmed, to exclude the possibility of the presence of indigo. This may be done by microchemical tests (the pigment is decolourised by alkali with the formation of brown ferric hydroxide) or by instrumental methods, such as energy-dispersive X-ray microanalysis (EDX), to confirm the presence of iron. As count rates for the principal iron peaks are quite low for Prussian blue, it is important to allow a long enough counting time in acquiring spectra to give a reliable result.<sup>17</sup>

### Early reports of the effects of light on the pigment

The reputation of Prussian blue as a durable pigment, rivalling ultramarine, was not maintained throughout the century or so that elapsed following the dramatic announcement of the pigment in 1710. At that time, because its ingredients included dried blood or other animal matter, Prussian blue was considered to be what would nowadays be called an organic pigment; such pigments, derived from plant or animal sources, were known to be fugitive. The chemist Peter Shaw commented in his public lectures, published in 1734, that because of the animal and vegetable matters used in its preparation the durability of Prussian blue might be suspected, were it not for the fact that the colour seemed to have been rendered stable, or 'fixed', by the method of preparation.<sup>18</sup>

Shaw's suspicions were justified for, by the middle of the century, writers of handbooks on painting and on artists' materials were no longer so enthusiastic in their praise for the pigment. In the first place, the claim in the 1710 advertisement that the pigment was stable to alkali was false: the pigment is rapidly

decomposed, forming a brown hydrated ferric oxide. This reaction takes place with lime, thus the pigment cannot be used in fresco.<sup>19</sup> The effects of light on the pigment had also become apparent. Antoine Pernety, in the practical treatise published with his dictionary of painting in 1757, wrote that the colour when used in oil painting tended to become greenish in time,<sup>20</sup> a change noted by later writers, including Heinrich Stöckel, who wrote a comprehensive handbook on oil painting in 1798, and Jean-François Merimée, the author of one of the most widely read works on oil painting.<sup>21</sup> Constant de Massoul, on the other hand, wrote that the iron in the colour tended to regenerate and become black.<sup>22</sup> Other writers merely described the colour as being impermanent.<sup>23</sup> Julius Caesar Ibbetson was a little more informative, writing, 'It will not stand very long in the sun.'<sup>24</sup>

It had also been noticed that the admixture of white, either as a result of the method of preparation (discussed below) or by the deliberate addition of white pigment, had some influence on the stability of the pigment. As the colour was so dark and intense, it was rarely used without the addition of some white. Robert Dossie, writing in 1758, stated that the darker varieties of the pigment were usually more permanent than the lighter (the variation in colour being caused by the presence or absence of an 'earth' — hydrated alumina — precipitated with the blue during the reaction), although they lacked brightness and were very purple. On the other hand, the lighter, brighter varieties were 'extremely subject to fly, or to turn to a greyish green'.<sup>25</sup> Stöckel thought that the addition of flake white to the pigment for use in oil caused no problem, but that the chalk or other additives present in ordinary lead white went yellow-green. He also wrote that if the pigment was to be used in oil, it was much improved by first treating it with concentrated sulphuric acid.<sup>26</sup> Other writers thought that lead white or other white extender pigments used in its place contributed to the change in colour of the Prussian blue.<sup>27</sup>

The curious tendency of Prussian blue decolorised by the action of light to regain its colour in the dark is vividly described by Franz Fernbach, the author of a book on oil painting, in 1834. Having decorated a rain shelter with pigments mixed with copal varnish and thinned with turpentine, he left it to dry in the sun. On his return some time later, he found to his horror that those areas painted with Prussian blue had faded almost completely. Rather than repaint them straightaway, he decided to wait until the next morning, when he was even more astonished to find the colour restored to its full strength. After this experience, he covered areas painted with Prussian blue with thick paper before leaving them in the sun and had no further trouble. He does not report,

however, how well the dried colour survived as time went by.<sup>28</sup>

The vacillating behaviour of Prussian blue under the influence of light was most systematically demonstrated by George Field. During the first quarter of the nineteenth century, he carried out experiments on the permanence of pigments, in both watercolour and oil medium, exposing identical samples to sunlight and 'to the foul air ... of a privy' for up to five weeks, until a wash of brasilwood or cochineal lake (both notoriously fugitive colours) had lost its colour; further identical samples were kept carefully folded in paper for comparison. Pigment samples, many obtained from London colourmen, were painted out at three levels of intensity: a thin glaze over white; a shade of intermediate strength; and as a thick layer. In oil, samples mixed with lead white were also included. Pigments were considered durable in proportion to the loss of colour they displayed in comparison with the lake pigment standard. His samples of Prussian blue were turned purple by the damp noxious air, and faded in the sun to varying degrees, regaining their colour when removed from the testing conditions.<sup>29</sup> In these particular tests Field did not comment on the tendency of the colour to go green, but in *Chromatography; or, A Treatise on Colours and Pigments and of their Powers in Painting*, published in 1835, he stated that it sometimes became greenish, a change he attributed to the development of a yellow iron oxide, and that its tints faded under the action of strong light. It was also, he wrote, a fluctuating pigment.<sup>30</sup>

### Early methods of preparation and the nature of the pigment

Field's experimental conditions appear rather less severe than modern testing conditions, yet the modern pigment seems to withstand these latter reasonably well.<sup>31</sup> It is necessary to ask, therefore, to what extent the modern pigment differs from the eighteenth- or early nineteenth-century version.

Modern Prussian blue exists in several different varieties, of which the best and most permanent is ferric ferrocyanide (iron(III) hexacyanoferrate(II)),  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$  (where  $x$  is 14–16), so-called insoluble Prussian blue. It is difficult to obtain pure, although it can be obtained (even in crystalline form) by the reaction between ferrous hydrogen cyanide,  $\text{H}_4[\text{Fe}(\text{CN})_6]$  and ferric chloride in hydrochloric acid. The common method of producing the pigment by mixing excess ferric chloride solution, or another iron(III) salt, with potassium ferrocyanide (or, strictly speaking, potassium hexacyanoferrate(II),  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ ) gives a voluminous, deep blue precipitate or colloidal suspension. The particle size of

the product is extremely fine; consequently, if precipitation is rapid, as is usually the case, variable amounts of potassium are incorporated in the complex and the product is a potassium iron(III) hexacyanoferrate(II). So-called soluble Prussian blue (supposedly the least permanent variety), a simplified formula for which is  $\text{KFe}[\text{Fe}(\text{CN})_6] \cdot \text{H}_2\text{O}$ , is produced by adding ferric chloride solution to excess potassium ferrocyanide, or by using 1:1 molar proportions of the two compounds. If this pigment is boiled with ferric chloride solution, the insoluble form is obtained. Turnbull's blue, which may also be obtained in soluble and insoluble forms and is reputed to have a permanence between that of the other two varieties, is obtained by the reaction of an iron(II) salt, such as ferrous sulphate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , with potassium ferricyanide (potassium hexacyanoferrate(III),  $\text{K}_3\text{Fe}(\text{CN})_6$ ). The product was thought to be ferrous ferricyanide, but Mössbauer spectroscopy has shown that it is identical in structure to the normal ferric ferrocyanide pigment.<sup>32</sup>

Nowadays the pigment is manufactured on an industrial scale by an indirect method, based on the reaction between ferrous sulphate and sodium ferrocyanide in the presence of ammonium sulphate to give a white insoluble product, Berlin white (ammonium iron(II) hexacyanoferrate(II),  $(\text{NH}_4)_2\text{Fe}[\text{Fe}(\text{CN})_6]$ ). This is converted to the ammonium-containing Prussian blue by oxidation with sodium bichromate or chlorate. The potassium-containing blue, although highly valued, is expensive to produce in bulk.<sup>33</sup>

The typical eighteenth-century method of preparing the pigment was far more curious. 'Nothing is perhaps more peculiar', wrote the French chemist Jean Hellot in 1762, 'than the process by which one obtains Prussian blue, and it must be owned that, if chance had not taken a hand, a profound theory would be necessary to invent it.'<sup>34</sup> The account of the method sent to John Woodward in 1724 was as follows. An alkaline salt (essentially potassium carbonate) was prepared by the detonation of crude potassium tartrate and potassium nitrate. This was mixed with dried blood and heated until the mixture ignited. When it ceased to burn, the black product was extracted with water and filtered off. The heated filtrate was mixed rapidly with hot solutions of ferrous sulphate and alum (aluminium sulphate, or potassium aluminium sulphate), producing much effervescence and a greenish precipitate. After filtering and washing, the precipitate was treated with hydrochloric acid to give the blue colour.<sup>35</sup>

The process was modified in various ways in the course of the century. John Brown demonstrated in 1724 that, while the iron in the vitriol was an essential ingredient, the alum (which was later recognised as also serving to neutralise excess alkali) appeared to serve principally as an extender: as Hellot said,

another white, if desired, would do as well.<sup>36</sup> Hellot also pointed out that complete calcination of the blood and rapid mixing were equally unnecessary.<sup>37</sup> Burnt hoofs or horns were found to serve almost as well as dried blood; different alkaline materials were used, including quick lime; conditions of calcination were altered; the proportions of the various ingredients were varied. Additional ingredients, such as red cochineal dyestuff, might be included: the reason for the inclusion of this particular additive was usually to give the pigment a more purple hue, but it has also some historical interest.<sup>38</sup> The acid, which dissolves out the alumina precipitated during the reaction, was sometimes omitted.<sup>39</sup>

Brown commented that it would be interesting to know how so singular a procedure came into being. It seems that the pigment was first obtained entirely by accident, according to the chemist Georg Ernst Stahl, who gave the earliest known account of its discovery in 1731. Diesbach, a Berlin colour maker, was preparing Florentine lake from cochineal dyestuff extracted with alum solution, to which a little ferrous sulphate had been added. Having run out of alkali with which to precipitate the red lake pigment, he acquired some from the alchemist Johann Dippel; on attempting to concentrate his colour, which appeared rather pale, he obtained a dark blue. Dippel realised that this unexpected result must have been caused by contamination of the alkali, which had previously been used in the repeated distillation of the 'animal oil' for which he was celebrated.<sup>40</sup>

While it was recognised that the animal matter — be it Dippel's 'animal oil', burnt hoofs or dried blood — played an essential part in the reaction, the nature of its contribution was not understood: in the 1720s chemistry as a theoretical science was insufficiently advanced. The animal matter was the source of the cyano- or cyanoferrate group, the  $-\text{CN}-$  or  $-\text{Fe}(\text{CN})_6-$  part of the pigment molecule, but at that time the understanding of compound formation was in its infancy and nitrogen had yet to be discovered. Potassium ferrocyanide itself was obtained from Prussian blue by the French chemist Pierre-Joseph Macquer in about 1752. He recognised it as containing the 'colouring principle', which he attributed to the presence of phlogiston, that curious hypothetical substance supposed to be the matter of fire and, by extension, of light, released during combustion.<sup>41</sup> It was not until the 1780s, however, with the publication of the work of the Swedish chemist Carl Wilhelm Scheele (better known perhaps for his discovery of oxygen and chlorine, and for the green copper arsenite pigment named after him) and that of Claude-Louis Berthollet, that some understanding of the structure of potassium ferrocyanide began to be obtained. Both recognised that it contained alkali and iron in



combination with what came to be called prussic acid and this breakthrough provided a basis for the research of the nineteenth century.<sup>42</sup> Even by 1795, the author of *A Practical Treatise on Painting in Oil Colours* was able to write that ‘Scheele and Berthollet have thrown much light on this subject, and have converted the old term of *phlogisticated alkali* into *Prussian acid*’.<sup>43</sup>

### The effects of the method of preparation on pigment durability

Manipulation of preparative conditions to obtain a pigment of the desired quality was thus based on trial and error for many years. As the process was relatively complex there were many possible variations that could be made and, as the discussion of the chemistry of the modern pigment has shown, different products could be obtained in consequence. It is very unlikely that the product was as chemically pure as would be expected today. Even the conditions of the precipitation itself — the temperature at which it takes place, the dilution of the reacting solutions and the speed of mixing — have an effect on the nature of the final product, particularly on physical properties such as particle size and colour. Obtaining a good quality Prussian blue was by no means straightforward. The problems described by one German manufacturer, Jacob Weber, at the end of the eighteenth century included incorrect calcination and a greyish, sulphur-containing coating forming on the final pigment, due, he thought, to impurities in the alkali.<sup>44</sup>

It is possible also that certain of these same variables in the method of preparation might have some influence on the stability of the final pigment. The varying potassium content is one possible factor to be considered. The soluble variety of Prussian blue was described by Church as the least permanent.<sup>45</sup> Mérimée, writing in 1830, related solubility of the pigment to potassium content,<sup>46</sup> but it was not until 1848 that Williamson published a method of obtaining a potassium-free pigment.<sup>47</sup> Another important factor could be the presence of other salts or contaminants arising as a result of the method of preparation. This was recognised at the time: Dossie commented, for example, that the cheaper grades of the pigment, used by decorators, were often contaminated by brown or yellow iron salts, also liable to be produced during the reaction. In a short while, work painted blue with this low-grade pigment turned olive green.<sup>48</sup> Many recipes also emphasised the need for thorough washing of the final pigment.

A far more important factor could be the presence of significant quantities of alumina, which was not always removed from the final pigment. This would serve as an extender, in the same way as adding a

quantity of white pigment to the pure pigment. The original announcement of the pigment stated that it was prepared in two grades, one lighter than the other and the darker being prepared from the lighter (see Appendix). Instructions were given in various sources for obtaining a darker blue by dissolving out the alumina: Stöckel thus converted a Berlin blue to Paris blue.<sup>49</sup> Alumina or other white pigments commonly used as extenders, such as white earths and barium sulphate, could also have been added deliberately.

It is interesting that there appears to have been a difference in quality between English Prussian blues and other European ones. As early as 1725, Geoffroy commented that the pigment prepared in London appeared more brilliant than that of Berlin;<sup>50</sup> Weber, after all his trials, was pleased to obtain a colour he reckoned to be as good as the English.<sup>51</sup> One of the most significant comments, however, is made by Bouvier, writing in 1827, who described the English pigment as being of higher quality than those made elsewhere. He claimed that, in watercolour, it lasted better than any other Prussian blue, even when exposed to the sun or mixed with white or other colours. It went green or brownish in oil, admittedly, but less so than the other blues. It was also darker in colour and, when burnt, made a less satisfactory brown.<sup>52</sup> He thought that the difference in the pigments was due to different methods of manufacture; Mérimée observed that the darker English blue contained less alumina.<sup>53</sup>

### Conclusion

From the occurrence of faded Prussian blue in some eighteenth-century oil paintings, it appears that the admixture of the pigment with a large quantity of white is a critical factor in its permanence. Documentary sources of the period provide evidence in support of this, but they also suggest that the Prussian blue in use then was, in any case, not a particularly durable pigment. The method of preparation was complicated and introduced a number of variable factors which may have had a bearing on the permanence of the eighteenth-century pigment. The method of manufacture in use today can be far more rigorously controlled, and altered at will to obtain a pigment with particular characteristics: colour, particle size and solubility can be modified as desired.

The second part of this study (to be published in a future issue of the *Technical Bulletin*) aims to provide the experimental evidence, on the basis of which the durability of eighteenth-century and modern pigments can be compared. Investigation of the constituents present in samples of Prussian blue dating from the eighteenth century onwards may throw some light on

the role played by such variables as the presence of alumina or other extenders, the proportion of potassium or, linked with this, the solubility of the pigment. The information from this analysis, together with the results of fading tests on a range of Prussian blues of different dates will, it is hoped, go some way towards explaining the behaviour of what Field so aptly described as this 'fluctuating pigment'.

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### Notes and references

1. J. Plesters, 'A preliminary note on the incidence of discolouration of smalt in oil media', *Studies in Conservation*, 14, 1969, pp. 62–74.
2. For a general account of the blue pigments available at the end of the seventeenth century see R. D. Harley, *Artists' Pigments c.1600–1835: A Study in English Documentary Sources*, 2nd edn., London 1982, pp. 43–75.
3. 'Notitia Coerulei Berolinensis nuper inventi', *Miscellanea Berolinensia*, I, 1710, pp. 377–8. The translation of the Latin original in the Appendix to the present paper is by Jo Kirby and Raymond White. For a discussion of the exact date of the discovery see Harley, op. cit., pp. 70–1.
4. 'Man hat heute zu Tage eine sehr schöne blaue Farbe in Berlin erfunden, so dem Ultramarin gleich, ja wohl gar dieselbe übertrifft': J. M. Cröker, *Der wohl anführende Mahler*, 3rd edn., Jena 1736; facsimile reprint, ed. U. Schiessl, Maander 1982, p. 117; see also the editor's comments, pp. VIII–IX. 1st edn. published in 1719; 2nd edn. 1729.
5. E.-L. Richter, Staatliche Akademie der Bildenden Künste, Stuttgart, private communication.
6. J. Woodward, 'Praeparatio caerulei Prussiaci ex Germania missa ad Johannem Woodward', *Philosophical Transactions*, XXXIII, no. 381, January–February 1724, pp. 15–17. Peter Shaw comments that the method was 'purchased as a very valuable Secret, both in England, Germany and elsewhere; but it is now got into several hands'. It is unclear whether he is referring to the years preceding 1724, but it is certainly possible: see P. Shaw, *Chemical Lectures publicly read at London in the years 1731 and 1732 ... for the improvement of Arts, Trades and Natural Philosophy*, London 1734, p. 182.
7. L. Faillant-Dumas, 'Watteau. Etude au Laboratoire de recherche des Musées de France', *Watteau: technique picturale et problèmes de restauration*, exhibition catalogue, Université Libre de Bruxelles, Brussels 1986, pp. 57–9. On the dating of the painting see M. Morgan Grasselli and P. Rosenburg, *Watteau 1684–1721*, exhibition catalogue, Washington/Paris/Berlin 1984–5, pp. 430–1.
8. E.-L. Richter, Staatliche Akademie der Bildenden Künste, Stuttgart, private communication. For the dating of the painting see Grasselli and Rosenburg, op. cit., p. 343.
9. Grasselli and Rosenburg, op. cit., p. 440. In the same catalogue, see also S. L. Fisher, 'The Examination and Treatment of Watteau's *Italian Comedians*', pp. 465–7, especially p. 466.
10. The pigment is described as durable in Winsor & Newton's *Notes on the Composition and Permanence of Artists' Colours*, Wealdstone [1981], pp. 10–12; in the *Daler-Rowney Catalogue of Fine Art and Graphics Materials*, Bracknell [1986], pp. 85, 87–8, it is classified moderately durable. See also Note 31.
11. Winsor & Newton, op. cit., pp. 11–12; R. Mayer, *The Artist's Handbook of Materials and Techniques*, 4th. edn., London 1982 (1987 reprint), pp. 87–9. The discussion of the stability of the pigment in A. H. Church, *The Chemistry of Paints and Painting*, 3rd edn., London 1901, pp. 215–16, although not modern, is still of interest.
12. J. A. Sistino, 'Ferriferrocyanide Pigments: Iron Blue', *Pigment Handbook*, ed. T. C. Patton, New York 1973, Vol. 1, pp. 404–5. The figures quoted refer to enamel formulations using a typical present-day Prussian blue (not necessarily that used for artists' pigments), ammonium ferric ferrocyanide, approximate formula  $\text{NH}_4\text{Fe}[\text{Fe}(\text{CN})_6]$ .
13. M. Davies, *National Gallery Catalogues: The British School*, 2nd edn., London 1959, pp. 36–7.
14. Davies, op. cit., pp. 34–5, 108–9. A brief discussion of the dating of *Mr and Mrs Andrews* appears in *The National Gallery Report*, London 1962, pp. 25–6.
15. M. Levey, *National Gallery Catalogues: The Seventeenth and Eighteenth Century Italian Schools*, London 1971 (1986 reprint), pp. 18–26, 33–6. See also D. Bomford and A. Roy, 'Canaletto's "Venice: The Feastday of S. Roch"', *National Gallery Technical Bulletin*, 6, 1982, pp. 40–3, and their article in this *Bulletin*, pp. 35–41.
16. Levey, op. cit., pp. 228–31; *The National Gallery Report*, London 1971, pp. 48–9.
17. S. Foister, 'The Portrait of Alexander Mornauer', *The Burlington Magazine*, CXXXIII, September 1991, p. 614, note 6. I am grateful to Ashok Roy for bringing this point to my attention.
18. Shaw, op. cit., p. 182. His comments on the pigment are reproduced, slightly edited, in *A*

*Compendium of Colors and other Materials used in the Arts dependent on Design*, London 1797, p. 18.

19. The effect of an alkaline environment on the pigment is discussed in E. Dayes, *The Works of the late Edward Dayes*, London 1805, pp. 300–1.

20. A.-J. Pernety, *Dictionnaire portatif de peinture, sculpture et gravure, avec un traité pratique des différentes manières de peindre*, Paris 1757, p. xciii.

21. H. F. A. Stöckel, *Praktisches Handbuch für Künstler, Lackir Liebhaber und Oeblfarben-Austreicher*, 2nd edn., Nuremberg 1799 (facsimile reprint, Aichstetten 1988), p. 31; J.-F.-L. Mérimée, *De la peinture à l'huile*, Paris 1830 (facsimile reprint, Puteaux 1981), p. 178. See also P.R. de C...C, *Traité de la peinture au pastel*, Paris 1788, pp. 150–1.

22. C. de Massoul, *A Treatise on the Art of Painting and the Composition of Colours*, London 1797, p. 182.

23. *The Art of Drawing and Painting in Water-colours*, London 1770, pp. 78–9; *A Compendium of Colors*, op. cit., p. 125.

24. J. C. Ibbetson, *An Accidence, or Gamut of Painting in Oil and Water Colours*, London 1803, p. 18.

25. R. Dossie, *The Handmaid to the Arts*, London 1758, Vol. I, pp. 77–8.

26. Stöckel, op. cit., p. 23.

27. *Nouveaux secrets des arts et métiers*, ed. M. Desbrières, Paris 1819, Vol. II, pp. 93–4.

28. F.X. Fernbach, *Ueber Kenntniss und Behandlung der Oebl-Farben*, Munich 1834, pp. 44–5.

29. G. Field, *A Journal of Practical Essays, Experiments and Enquiries, 1806*, ff. 39X, 39v; *Examples and Anecdotes of Pigments. Practical Journal, 1809*, ff. 300v, 316–17. Field Manuscripts, Field/2 and Field/6, photographic copies, Courtauld Institute Library, London.

30. G. Field, *Chromatography; or, A Treatise on Colours and Pigments and of their Powers in Painting*, London 1835, pp. 111–12.

31. Daler-Rowney state that pigment samples are exposed to sunlight for 500 hours, between May and September; for their testing conditions see the *Daler-Rowney Catalogue of Fine Art and Graphics Materials*, op. cit., p. 88. A sample of Winsor & Newton powder pigment, modern, but of unknown date, painted out as a wash of moderately intense colour in aqueous gum arabic and exposed to a constant illumination of 10,000 lux, supplied by Thorn artificial daylight fluorescent tubes, for about six months showed no significant colour change. On this evidence, one would assume that, indeed, Prussian blue was a reasonably durable pigment under normal circumstances.

32. A. Ludi, 'Prussian Blue, an Inorganic Evergreen', *Journal of Chemical Education*, 58, 12, 1981, p. 1013; A.G. Sharpe, *The Chemistry of Cyano Complexes of the Transition Metals*, London 1976, pp. 121–6; A. Ludi, 'Descriptive Chemistry of Mixed-Valence Compounds',

*Mixed-Valence Compounds: Theory and Applications in Chemistry, Physics, Geology and Biology*, ed. D. B. Brown, Dordrecht, London etc. 1980, pp. 39–44; see also Church, op. cit., pp. 213–15.

33. Sistino, op. cit., pp. 401–6; N. Heaton, *Outlines of Paint Technology*, 3rd edn., London 1948, pp. 154–8; J. S. Remington, and W. Francis, *Pigments: Their Manufacture, Properties and Use*, London 1954, pp. 94–9; *Inorganic Pigments: Manufacturing Processes*, ed. M. H. Gutcho, Park Ridge 1980, pp. 433–9.

34. J. Hellot, 'Sur la préparation du Bleu de Prusse', *Histoire de L'Académie Royale des Sciences*, Année MDCCLVI, 1762, p. 53: 'Rien n'est peut-être plus bizarre que le procédé par lequel on obtient le bleu de Prusse, & il faut avouer que si le hasard ne s'en est pas mêlé, il a fallu une profonde théorie pour l'imaginer.'

35. Woodward, op. cit., pp. 15–17. English translations of this method appear shortly afterwards; see, for example, Shaw, op. cit., pp. 180–2; J. Hoofnail, *The Painter's Companion, or, A Treatise on Colours*, London 1738, pp. 59–61. For translations into French see, for example, E.-F. Geoffroy, 'Observations sur la préparation du Bleu de Prusse, ou de Berlin', *Histoire de L'Académie Royale des Sciences*, Année MDCCXXV, 1727, pp. 155–7. The original recipe and an English translation appear in H. M. Powell, 'The Beginnings of Co-ordination Chemistry', *Proceedings of the Chemical Society*, March 1959, pp. 73–5.

36. J. Brown, 'Observations and Experiments upon the Foregoing preparation', *Philosophical Transactions*, XXXIII, no. 381, January–February 1724, pp. 17–24.

37. Hellot, op. cit., pp. 56–7.

38. See, for example, Hoofnail, op. cit., p. 61; Cröker, op. cit. pp. 535–6.

39. See, for example, Dossie, op. cit., pp. 78–80; Hellot, op. cit., pp. 57–9; Stöckel, op. cit., pp. 226–7, 240; M. Le Pileur d'Apligny, *Traité des couleurs matérielles*, Paris 1779, pp. 36–8; L. Marcucci, *Saggio analitico-chimico sopra i colori minerali*, 2nd edn., Rome 1816, pp. 54–7.

40. G. E. Stahl, *Experimenta, Observationes, Animadversiones, CCC Numero, chymicae et physicae*, Berlin 1731, pp. 280–3. There are points in this account which are open to question or speculation: if it is to be believed, one must presume that the ferrous sulphate had been added to deepen or 'sadden' the colour of the dyestuff. As far as lake pigment recipes are concerned, this is not common practice at this date: additives to make the colour more scarlet are far more likely. A slightly different, but no less bizarre, account is given by the chemist P. F. Tingry, *Traité théorique et pratique sur l'art de faire et d'appliquer les vernis*, Geneva 1803, Vol. II, p. 40. In his version, Dippel, having thrown various waste alkalis, previously

used for the distillation of 'animal oil', into his courtyard, observed to his surprise that several of the paving stones had become covered with a brilliant blue colour. He then remembered that he had previously discarded some iron sulphate residues in the same place and conducted further research into the preparation of the colour. One wonders how far Tingry is being wise after the event in this story. Dippel's 'animal oil' was later found to contain pyridine and other nitrogen-containing organic compounds.

41. P.-J. Macquer, 'Examen chymique du Bleu de Prusse', *Mémoires de mathématique et de physique de l'Académie Royale des Sciences*, Année MDCCLII, 1756, pp. 60–77

42. C. W. Scheele, *The Collected Papers of Carl Wilhelm Scheele*, trs. L. Dobbin, London 1931, pp. 238–55; C.-L. Berthollet, 'Mémoire sur l'acide prussique', *Mémoires ... de l'Académie Royale des Sciences*, Année MDCCLXXXVII, 1789, pp. 148–62. See also J.R. Partington, *A History of Chemistry*, Vol. III, London 1962 (1970 reprint) and the references therein. For a summary of the early history of the chemistry of Prussian blue, see L. J. M. Coleby, 'A History of Prussian Blue', *Annals of Science*, IV, 1939, pp. 206–11.

43. *A Practical Treatise on Painting in Oil Colours*, London 1795, p. 53

44. J. A. Weber, *Chemische Erfahrungen bey meinem und anderen Fabriken in Deutschland*, Neuwied 1793, pp. 134–65, 189–200.

45. Church, op. cit., pp. 213–15.

46. Mérimée, op. cit., p. 178.

47. A. W. Williamson, 'On the Blue Compounds of Cyanogen and Iron', *Memoirs and Proceedings of the Chemical Society*, 3, 1848, pp. 125–40.

48. Dossie, op. cit., p. 82.

49. Stöckel, op. cit., p. 240.

50. Geoffroy, op. cit., p. 154

51. Weber, op. cit., pp. 195–6.

52. P.-L. Bouvier, *Manuel des jeunes artistes et amateurs en peinture*, Paris 1827; 2nd edn., 1832, pp. 39–40, 49–52.

53. Mérimée, op. cit., pp. 203–4.

## Appendix

### 'Notitia Coerulei Berolinensis nuper inventi', *Miscellanea Berolinensia*, 1 (1710), pp. 377–8.

'Notice of Prussian Blue lately invented'

Painters who mix oil with their colours have few that represent blue, and those such that, rightly, they wish for [some] more satisfactory. Of the common [blues], certainly, one does not reject mixture with the oil, but does not last for a long time in the work: it becomes greenish, somewhat pale, rust-coloured or distinctly dirty. Another is indeed constant and beautiful enough, but sandy; and this defect, which is inconvenient to the fine work of a skilled master, cannot be removed if the space of a year were to be consumed in grinding it. The best of all, which ordinarily they call Ultramarine or Azure, which is produced from lapis lazuli, not only deters many by its price, but also does not freely permit the addition of other colours; and this last is able to show its beauty only in the light parts: it is useless [*in utilis*]<sup>1</sup> in the shadows.

This just desire of craftsmen, the blue colour, which was invented here in Berlin several years ago and [which] now, after different, most careful considerations, appears boldly in the public eye, can certainly alleviate, if not satisfy. For instance, it has none of these inconveniences. In oil it shows its chief splendour. In truth everywhere, in water, oil and other liquids with which one can paint, it is found to be durable in the highest degree. That nitric acid [*aqua fortis*], as it is called by chemists, which erodes or dissolves everything, does not change it so much, far less destroy it, as render it brighter. And as certain blue colours can be employed in encaustic painting (*Schmelzwerck/émail*)<sup>2</sup> and, so it is said, are not destroyed by drying by fire, so this new colour strongly resists caustic liquids [*igni humido*]<sup>3</sup> (which name those acids and all destructive agents can rightly be given); which difficulty it, out of all types of colours, can endure. This [colour] fears even less the more common investigations of painters: for example, the juice squeezed from citrus fruits, etc. It is not changed [when] in place [*in loci*]<sup>4</sup> either by the air or by change in the weather. It survives in quick lime and in that white which distinguishes gold from a gem.<sup>5</sup> Just as it was formed out of the most finely divided materials, so it can be ground into the finest powder. And where it is not sufficiently reduced by the first stage [in the process], it may be completed by a second or a third; however, by these separate stages having thus been made dry, it can be wetted again by pure water. Indeed, for that reason [*eo*],<sup>6</sup> by these means only, it is usual to complete this work in that art of painting in the smallest degree, which they call

miniature, the more skilfully, as they wish. Or other painters, who mix colours on a board, can reduce it with a knife with little trouble. Because of this [afore-mentioned] fineness, it covers wonderfully areas that are spread with a brush and it can be extended by other colours. Besides, not only is it able to be covered over by less obscuring colours of its kind and is able to set off things that stand out more, but also it can shade in folds, hollows and the greater depths of the picture.

This [colour] is of two kinds: the one dark and more suited to expressing shadow; the other light, not mixed with ceruse or with another white, but being in this state at once, at its first appearance.<sup>7</sup> The darker type of this colour is made from the lighter and becomes as if reduced, or, as they say, becomes concentrated. Painters of lesser kinds, who customarily measure [out] this colour for the purpose of common mixing, rarely desire the lighter variety: [they] search for the darker alone and, mixing white with it, add light by degrees. Those whose eyes are more discerning in fact immediately perceive [that] a colour, which rises to a lighter grade out of its darkness by the admixture of white, has not produced so much light and attractiveness in its being as that which Nature has produced in a weaker form.

For the rest, it is harmless: nothing here is arsenical; nothing contrary to health, but rather a medicine. Without danger, those things which are made from sugar can be painted in this colour and eaten. Beginners of painting can safely draw through their lips the brushes with which they spread their panels;

which they will do with other paints not without danger to life. The price, finally, by which it is procured, scarcely approaches a tenth part of [that of] the dearest Ultramarine. And the supply of this, which in Berlin can be had at the Bookseller of the Royal Society of Sciences, is as much as the prodigal hand of craftsmen can desire for the purposes of adorning their work.

## Notes

1. *In utilis* makes very little sense. It seems probable that this is a misprint for *inutilis*, 'useless'.
2. *Schmelzwerck* and *émail* both mean enamel. This clause should be taken to refer to blue pigments that are not destroyed by heating in a general sense.
3. Literally, 'liquid fire'. 'Caustic' here signifies liquids that produce a burning, but not necessarily alkaline, effect.
4. 'In position' or 'in places', i.e., when the pigment is painted out in its place on the picture. The word *loci* may be a misprint for *locis*, or possibly *loco*.
5. It is not clear what this white may be.
6. The word *eo*, in the locative and ablative cases, can be used as an adverbial case, referring to a cause or reason given previously, in this case the fact that the pigment wets easily; this means that it can be used skilfully in miniature painting. One could infer from these two sentences that, in watercolour, washes are easily made from the pigment.
7. In other words, it appears as a lighter colour as manufactured.