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Investigation of 19th and early 20th century Prussian blue production methods and their influence on the pigment composition and properties

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ABSTRACT

Several degradation phenomena, including cracking and paint loss have been observed in Prussian blue oil paint strokes in Vincent van Gogh’s paintings. To understand the influence of the pigment on these phenomena, 19th and early 20th century preparation and purification methods of the Prussian blue pigment and their influence on its composition and properties were studied using contemporary sources. Recipes for replication were selected based on their prevalence, the detail in their description, as well as the quality ascribed to the prepared pigments. Two direct recipes, two indirect recipes, a conversion from soluble to insoluble Prussian blue and two 18th century recipes were used for the reproduction of Prussian blue, including the historical purification methods. The prepared pigments were analysed using ATR-FTIR, XRD and SEM-EDX. Differences between the pigments were found in the presence of certain contaminants, as well as in the size and shape of the pigment particles. These contaminants included nitrates and carbonates. The differences in particle characteristics were found to result in differences in shades and tinting strengths of the pigments and prepared oil paints.

1. Introduction

Discovered in or shortly after 1704, Prussian blue is considered to be one of the first modern synthetic pigments [1,2]. Due to its intense colour and low cost of production, the pigment quickly became a popular artist’s pigment. However, its permanence was questioned as early as halfway through the 18th century, with reports of its colour turning green or fading [2,3]. The fading and colour change of Prussian blue have been extensively studied, both when used in oil paintings and in other media, including as a watercolour on paper and as a dye for textiles [2,4–9]. In oil paintings, Prussian blue has been found to be light-fast when used pure but to fade increasingly when mixed with white pigments or extenders in higher ratios [1–3,6,8,9]. It was commonly mixed with, for example, zinc white, lead white, or alumina, which allowed for a lighter shade of blue to be used in paintings. Prussian blue has also been used in green paints in mixtures with yellow pigments, such as chrome yellow [1].

Besides the colour change of Prussian blue paint, other degradation phenomena have also been observed in oil paintings in areas where Prussian blue is used. During the examination of several of Vincent van Gogh’s paintings, certain degradation phenomena were often found to be present in the very dark blue, almost black paint strokes. The observed issues include cracking, delamination and paint loss, as well as solvent sensitivity of the Prussian blue paint. Initial X-ray fluorescence spectroscopy (XRF), scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX) and optical microscopy analyses have confirmed that these paint strokes consist of almost pure Prussian blue oil paint, mixed with very little or no lead white or zinc white.

The cause of the observed degradation of Prussian blue oil paints is not yet understood, also due to the currently limited knowledge of the Prussian blue pigments used in Van Gogh’s time. For example, the influence of the preparation and purification processes for Prussian blue pigments in the mid-19th to early 20th century on the final composition and properties of the pigment used in artists’ paint at that time has not yet been investigated. It may be expected that different manufacturing
processes will influence the particle characteristics as well as the chemical composition of the produced Prussian blue. For instance, Samain et al. have reported that the particle size of Prussian blue pigments and the local disorder in their structure appear to be strongly dependent on the preparation method, influencing their hue, tinting strength, and hiding power [10]. However, they focused on modern preparation methods and did not investigate 19th and 20th century recipes.

In the current paper, research into historical sources is combined with replications of the described preparation and purification methods. The prevalence of certain recipes as well as their ease of replication were used to determine what procedures were likely followed in Van Gogh’s time for the preparation of Prussian blue. In addition, chemical analysis of the created pigments and assessment of the morphology of the pigment particles are performed to better understand the influence of 19th and early 20th century preparation and purification methods on the final pigment composition and properties.

2. Background and historical recipes

2.1. Prussian blue pigments and their discovery

Prussian blue pigments are mixed-valence iron(III) hexacyanoferrate (II) complexes, which are usually described by one of two chemical formulas, $\text{Fe}_3\text{III} \left(\text{Fe}^{\text{II}}\text{CN}_6\right)_6 \cdot x\text{H}_2\text{O} (x = 14–16)$ for so-called insoluble and $\text{KFe}_3\text{III} \left(\text{Fe}^{\text{II}}\text{CN}_6\right)_6 \cdot x\text{H}_2\text{O}$ (with varying $x$) for soluble Prussian blue [1–3]. In fact, both of these compounds are insoluble, but the potassium-containing variant more easily forms colloidal suspensions. Instead of potassium, the soluble variant may also contain other cations, such as sodium or ammonium. The three-dimensional structures of Prussian blue are generally accepted and given as the models shown in Fig. 1. Soluble Prussian blue is depicted according to the model of Ludi et al. from 1977 [12], in which a hexacyanoferrate(II) vacancy is present. In reality, the quick precipitation during the synthesis of Prussian blue pigments leads to the presence of vacancies in both the soluble and insoluble variants and in these cases its stoichiometry deviates from the ideal Prussian blue formula, and neither structural model is fully correct [13,14].

At the time of its initial discovery around 1704, attributed to the pigment maker Diesbach in Berlin, little was known about the chemical composition of Prussian blue [1–3]. It is said that Diesbach was attempting to make a cochineal lake, but instead obtained a blue-coloured pigment [15,16]. The subsequently developed method for the synthesis of Prussian blue was initially kept secret, but in 1724 it was published by John Woodward in *Philosophical Transactions* [17]. The published recipe starts with the heating of potassium nitrate and potassium bitartrate to obtain what is essentially potassium carbonate (Fig. 2). Dried blood is then added and the mixture is heated until it burns. The dried blood serves as a source of nitrogen, and, although not yet understood at this time, its thorough heating results in the formation of hydrogen cyanide, which reacts with potassium carbonate to form potassium cyanide [16]. The still hot mixture is then boiled in water and the solids are filtered out. The solution obtained in this way, sometimes called blood lye, consists mostly of potassium cyanide, but also already some potassium ferrocyanide and the remainder of the potassium carbonate. Separate solutions of alum (potassium aluminium sulphate) and iron(II) sulphate are then added to the blood lye, resulting in the formation of a green precipitate. In an immediate reaction to the synthesis of Woodward, published in the same volume of *Philosophical Transactions*, the chemist John Brown demonstrates that alum is not required for the formation of Prussian blue [18]. It was later realised that alum neutralises excess alkali, forming hydrated alumina, which functions mostly as an extender. The green precipitate is obtained via filtration using a linen cloth, treated with hydrochloric acid and subsequently washed. Hydrochloric acid removes the hydrated alumina that forms
Table 1
Overview of general recipes found in 19th and early 20th century sources and the names commonly given to pigments produced following those recipes.

<table>
<thead>
<tr>
<th>General recipe</th>
<th>Special names</th>
<th>Sources</th>
</tr>
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<tbody>
<tr>
<td>Starting from animal matter with potassium carbonate or (crude) potassium ferrocyanide solution, mixed with iron (II) sulphate and alum solution. Sometimes followed by hydrochloric acid treatment.</td>
<td>Cheaper blues by J. C. Booth (1853, 1890)</td>
<td>A. J. Cooley (1845, 1856, 1880, 1892) [23-26]; G. W. Francis (1848) [31]; J. C. Booth (1853, 1890) [20,21]; J. G. Gentele (1860) [27]; J. Riffault des Hêtres et al. (1874) [32]; R. Wagner (1889, 1897) [28,29]; J. Bersch (1901) [22]</td>
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<td></td>
<td>Old method for Prussian blue by J. G. Gentele (1860) and R. Wagner (1889, 1897)</td>
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<td></td>
<td>Mineral blue, when containing large amounts of alumina, by R. Wagner (1889, 1897) and J. Bersch (1901)</td>
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<tr>
<td></td>
<td>Insoluble Prussian blue by A. J. Cooley (1892)</td>
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<tr>
<td>Starting with acid treatment of crude potassium ferrocyanide solution (blood lye), then iron(II) sulphate addition.</td>
<td>Paris blue by A. J. Cooley (1845, 1856, 1880, 1892)</td>
<td>A. J. Cooley (1845, 1856, 1880, 1892) [23-26]; G. W. Francis (1848) [31]</td>
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<tr>
<td>Mixing with various white compounds after or during synthesis.</td>
<td>Mineral blue by J. G Gentele (1860), J. Riffault des Hêtres et al. (1874) and J. Bersch (1901)</td>
<td>J. G. Gentele (1860) [27]; J. Riffault des Hêtres et al. (1874) [32]; J. Bersch (1901) [22]; J. G. Bearn (1924) [35]; R. Gettens and G. Stout (1942) [36]</td>
</tr>
<tr>
<td></td>
<td>Antwerp blue by J. Riffault des Hêtres et al. (1874), J. Bersch (1901), J. G. Bearn (1924) and R. Gettens and G. Stout (1942)</td>
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<td>Brunswick blue by J. Bersch (1901) and J. G. Bearn (1924)</td>
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<tr>
<td></td>
<td>Celestial blue by J. G. Bearn (1924)</td>
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</tr>
<tr>
<td>Addition of an iron(III) salt to an excess of potassium ferrocyanide.</td>
<td>Soluble Prussian blue by J. C. Booth (1853, 1890), A. J. Cooley (1856, 1880, 1892), A.H. Church (1890, 1915) and J. Bersch (1901)</td>
<td>J. C. Booth (1853, 1890) [20,21]; A. J. Cooley (1856, 1880, 1892) [24-26]; A. H. Church (1890, 1915) [36,37]; J. Bersch (1901) [22]</td>
</tr>
<tr>
<td></td>
<td>J. Bersch includes the addition of sodium sulphate, to prevent Prussian blue from dissolving</td>
<td></td>
</tr>
<tr>
<td>Addition of potassium ferrocyanide to an iron(III) salt.</td>
<td>Neutral Prussian blue by J. C. Booth (1853, 1890) and R. Wagner (1889, 1897)</td>
<td>J. C. Booth (1853, 1890) [20,21]; R. Wagner (1889, 1897) [28,29]</td>
</tr>
<tr>
<td>Addition of potassium ferrocyanide to an excess of iron(III) salt.</td>
<td>Insoluble Prussian blue by A. H. Church (1890, 1915)</td>
<td>A. H. Church (1890, 1915) [36,37]; J. Bersch (1901) [22]</td>
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<tr>
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<td>Insoluble Chinese blue by J. Bersch (1901)</td>
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<tr>
<td>Addition of an iron(II) salt to potassium ferricyanide.</td>
<td>Turnbull’s blue by A. J. Cooley (1845, 1856, 1880, 1892), J. C. Booth (1853, 1890), J. G. Gentele (1860), J. Riffault des Hêtres et al. (1874), R. Wagner (1889, 1897), J. Bersch (1901) and J. G. Bearn (1924)</td>
<td>A. J. Cooley (1845, 1856, 1880, 1892) [23-26]; J. C. Booth (1853, 1890) [20,21]; J. G. Gentele (1860) [27]; J. Riffault des Hêtres et al. (1874) [32]; R. Wagner (1889, 1897) [28,29]; A. H. Church (1890, 1915) [36,37]; J. Bersch (1901) [22]; J. G. Bearn (1924) [35]</td>
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<td></td>
<td>Paris blue by J. C. Booth (1853, 1890) and J. Riffault des Hêtres et al. (1874)</td>
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<td>Soluble Prussian blue, if an excess of potassium ferricyanide is used, by A. H. Church (1890, 1915)</td>
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<td></td>
<td>Gmelin’s blue by J. G. Bearn (1924)</td>
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Table 1 (continued)

<table>
<thead>
<tr>
<th>General recipe</th>
<th>Special names</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Addition of an iron(II) salt to potassium ferrocyanide, followed by air oxidation.</td>
<td>Basic Prussian blue by J. C. Booth (1853, 1890) and R. Wagner (1889, 1897)</td>
<td>J. C. Booth (1853, 1890) [20,21]; A. J. Cooley (1856, 1880) [24,25]; R. Wagner (1889, 1897) [28,29]</td>
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<tr>
<td></td>
<td>Soluble and basic Prussian blue by A. J. Cooley (1856, 1880)</td>
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</tr>
<tr>
<td>Addition of an iron(II) salt to potassium ferrocyanide, followed by other oxidation methods.</td>
<td>Paris blue by A. J. Cooley (1845, 1856, 1880, 1892), J. C. Booth (1853, 1890) and J. Riffault des Hêtres et al. (1874)</td>
<td>A. J. Cooley (1845, 1856, 1880, 1892) [23–26]; J. C. Booth (1853, 1890) [20,21]; J. G. Gentele (1860) [27]; J. Riffault des Hêtres et al. (1874) [22]; R. Wagner (1889, 1897) [28,29]; A. H. Church (1890, 1915) [36,37]; J. Bersch (1901) [22]; J. G. Bearn (1924) [35]; J. Bersch (1901) [22]; J. G. Bearn (1924) [35]; R. Gettens and G. Stout (1942) [38]</td>
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<td></td>
<td>Turnbull’s blue by J. C. Booth (1853, 1890) and J. Riffault des Hêtres et al. (1874)</td>
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<td>Commercial Prussian blue by A. H. Church (1890, 1915)</td>
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<td>Chinese blue by J. Bersch (1901) and, if hydrochloric acid and potassium chlorate are used for the oxidation step, by J. G. Bearn (1924)</td>
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<tr>
<td></td>
<td>Bronze blue, if hydrochloric acid and calcium hypochlorite are used for the oxidation step, by J. G. Bearn (1924)</td>
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<tr>
<td>Digestion of Prussian blue in acid.</td>
<td>Soluble Prussian blue by R. Wagner (1889, 1897) and J. G. Bearn (1924)</td>
<td>R. Wagner (1889, 1897) [28,29]; J. G. Bearn (1924) [35]</td>
</tr>
<tr>
<td>Boiling soluble Prussian blue with iron(III) chloride.</td>
<td>Insoluble Prussian blue by A. H. Church (1890, 1915) and A. J. Cooley (1892)</td>
<td>A. H. Church (1890, 1915) [36,37]; A. J. Cooley (1892) [26]</td>
</tr>
<tr>
<td>Mixing iron(III) chloride with ferrocyanic acid.</td>
<td>Insoluble Prussian blue by A. H. Church (1890, 1915)</td>
<td>A. H. Church (1890, 1915) [36,37]</td>
</tr>
<tr>
<td>Oxidising Turnbull’s blue using chlorine water or nitric acid.</td>
<td>Insoluble Prussian blue by A. H. Church (1890, 1915) and A. J. Cooley (1892)</td>
<td>A. H. Church (1890, 1915) [36,37]; A. J. Cooley (1892) [26]</td>
</tr>
<tr>
<td>Mixing Prussian blue with potassium ferrocyanide and boiling or digestion in water.</td>
<td>Soluble Prussian blue by A. J. Cooley (1892)</td>
<td>J. G. Gentele (1860) [27]; A. J. Cooley (1892) [26]</td>
</tr>
</tbody>
</table>

during the synthesis process, and less or more acid can be used to gain a pigment with a lighter or deeper blue colour. Similar recipes were later published, for example by Dossie in 1758 in his *Handmaid to the Arts* [19]. Dossie discusses that Woodward’s recipe will “produce an equally fine colour”, although the ratios of the ingredients in his own recipe are “more accurately adapted to each other”.

It took more than a century, after the initial discovery of Prussian blue, till the chemical processes resulting in its formation and its chemical composition were really understood. New recipes for the production of the pigment started from potassium ferrocyanide or potassium ferricyanide, although the latter was less used due to its higher cost [20–22]. In most of the 19th century, these starting materials themselves were still obtained from animal matter, but pigment makers could buy them relatively pure and in bulk [20–29]. Recipes for the production of Prussian blue at the time were not always clearly classified, and may be difficult to assign due to the many synonyms used for the pigment. Here, the recipes
will be classified according to their pathway, either direct or indirect, and
to the ratio between starting materials, leading to so-called
soluble or insoluble Prussian blue.

In the direct synthesis, an iron(III) salt is mixed with a ferrocyanide
salt, like $K_3[Fe(CN)_6]$, to obtain Prussian blue $[1,2]$. Alternatively, an
iron(II) salt can be combined with a ferrocyanide salt, $K_3[Fe(CN)_6]$, to
obtain the same complex. During the 19th century, it was still believed
that the latter method resulted in an iron(II) hexacyanoferrate(III)
complex, named Turnbull’s blue, but this was later shown to be incorrect
using Mössbauer spectroscopy $[30]$. Both of these direct methods result
in the formation of an iron(III) hexacyanoferrate(II) complex.

The indirect synthesis method consists of two steps, starting with the
reaction between an iron(II) salt and a ferrocyanide salt, which results in the
formation of Berlin white, $K_2Fe[Fe(CN)_6]$ $[1,2]$. This compound is slowly
oxidised in air to give Prussian blue, but usually an oxidising agent is used to
complete this step. Modern industrial processes for the synthesis of Prussian
blue are based on this indirect method. Both direct and indirect modern
synthesis methods are generally expected to lead to fewer impurities in the
final product compared to the recipes developed in the 18th century,
resulting in a more stable and permanent pigment. However, Prussian blue
made using any method has a very small particle size and colloidal nature,
which makes it difficult to completely remove impurities from the final
product, even when modern synthesis methods are used $[1,2]$.

The relative amounts of starting materials in either synthesis
pathway can be adjusted to obtain either soluble or insoluble Prussian blue:
with a 1:1 ratio or an excess of ferrocyanide salt leads to the formation
of soluble Prussian blue, while the use of an excess of iron salt produces
the insoluble variant $[2,3]$. However, even if insoluble Prussian blue is
the desired product, the quick precipitation of Prussian blue particles in
a direct synthesis pathway still leads to the inclusion of some potassium

2.2. Preparation of Prussian blue in the 19th and early 20th century

An overview of the general recipes for the production of Prussian
blue found in 19th and early 20th century sources is provided in Table 1.
The recipes are listed alongside the names given to pigments prepared
according to these recipes, as well as the historical sources in which the
recipes were found. The names included in the table are only those that
were found to have mostly been used for specific preparations of the
pigment, and not the more general names that were used to address
pigments prepared according to various recipes, such as Berlin or
Prussian blue.

In the early and mid-19th century, many of the reported recipes still
started with the production of the blood lye solution from nitrogen-rich
animal matter and potassium carbonate $[23,27,31,32]$. These recipes
generally involve the addition of a solution containing both iron(II)
sulphate and alum, leading to the inclusion of hydrated alumina in the
final pigment. Indeed, previous analyses of pigments from the early 19th
century and before show that this is a characteristic of Prussian blue
prepared following this older recipe, starting from animal matter $[3,7]$.
Pigments prepared in this way have also been found to have a larger and
more irregular particle size, often plate- or flake-like, when examined
using optical microscopy $[33,34]$. In the course of the 19th century, several recipes were developed
starting immediately with the pure potassium ferrocyanide salt $[20–29]$.
At this point, the salt itself is still obtained from nitrogen-containing
matter and potassium carbonate, but the resulting blood lye is evapo-
rated and the obtained salt is recrystallised to obtain it in its pure form.
However, it has to be noted that the presence of potassium sulphate as a
difficult-to-remove impurity is discussed in several sources, indicating
that it was still difficult to obtain the potassium ferrocyanide crystals
entirely pure $[22,27]$. Recipes described to give a cheaper kind of blue
with inferior quality still include the addition of an alum solution,
resulting in a lighter blue pigment $[20,21,32,35]$. Instead of this addi-
tion during the synthesis, other white extenders are sometimes added
after preparation of the pigment, while still wet $[22,27,35]$. Possible
additions include starch, baryte, gypsum and kaolin. These cheaper blue
pigments were commonly called Antwerp, mineral or Brunswick blue.
They can also contain zinc oxide or magnesium, added as their respective
metal salts during the synthesis.

Recipes for the production of a purer Prussian blue given in 19th and
early 20th century sources are generally indirect methods, consisting of
the combination of an iron(II) salt with potassium ferrocyanide followed
by oxidation of the precipitated Berlin white to obtain Prussian blue.
Various oxidation processes were used at the time for the latter step.
Several direct methods are also given, which are usually deemed to lead
to inferior quality pigments. In contrast, the direct method for the production
of so-called Turnbull’s blue, from an iron(II) salt and potassium ferrocy-
nide, is said in various sources to be a very pure pigment of good quality
and beautiful colour $[20,21,23–26,32]$. These excellent properties
of Turnbull’s blue are said to be overshadowed by the cost of its starting
material potassium ferrocyanide, and it is often noted to be too expensive
to follow the recipe for its production $[20–22]$. In the 19th century,
Turnbull’s blue was still believed to be an iron(II) hexacyanoferrate(III)
complex and thus different from Prussian blue, an iron(III) hexacyanoferrate
(II) complex. It was not yet known that the two compounds are identical, as
was later proven using Mössbauer spectroscopy $[30]$. In the studied
sources, Turnbull’s blue is almost always used to refer to a pigment pre-
pared directly from an iron(II) salt and potassium ferrocyanide, but a
pigment prepared using this method is sometimes also called Paris blue.
Additionally, the name Paris blue is also given to pigments made following
an indirect method. In general, the names Turnbull’s blue, Paris blue and
also Chinese blue appear to have been used for what was considered to be
the best qualities of Prussian blue pigments.

The distinction between soluble and insoluble Prussian blue was also
made during the 19th century, particularly in sources towards the end of
the century. Soluble Prussian blue, made either from a direct or indirect
method with an excess of potassium ferrocyanide or ferricyanide, is
sometimes said to be less stable and less permanent than insoluble
Prussian $[22,35–37]$. However, these sources also consider the insoluble
variant to be free of any potassium, which is highly unlikely. Soluble
Prussian blue is said to be converted into insoluble Prussian blue when
boiled with an iron(III) salt, usually iron(III) chloride $[26,36,37]$. On
the other hand, several recipes for the digestion of insoluble Prussian blue in
acid to convert it to the soluble variant are also given $[28,29,35]$. The
dissolution, or more accurately dispersion, of soluble Prussian blue can
be prevented through the addition of a salt. The washing of the soluble
pigment is therefore said to be never fully completed, since this would
make it very difficult to separate the pigment from the solution unless
new salt is added.

As discussed before, the direct method for the production of Turn-
bull’s blue, from an iron(II) salt and potassium ferricyanide, is said to
lead to a high-quality pigment, but is considered to be too expensive.
Indirect methods are often acknowledged to be cheaper alternatives to
obtain an equally fine quality pigment, usually called Paris or Chinese
blue, and it is said that these methods were used for the production of
commercial Prussian blue pigments. They all start from the combination
of potassium ferrocyanide and iron(II) sulphate solutions, but vary in the
following oxidation step to convert the white precipitate to Prussian
blue. What seems to be agreed upon is the requirement for quick
oxidation, to prevent any oxidation by air, which is said to result in a
lower quality pigment in terms of beauty and intensity of its colour $[27,$
$32,35]$. One recipe that is commonly reported is that of Hochstättener
for Paris or Chinese blue, where the white precipitate is treated with sulfuric
and hydrochloric acid and allowed to stand for several hours $[20–26]$.
The mixture is then treated with calcium hypochlorite solution, allowed
to stand for several more hours, and is finally thoroughly washed or
treated with dilute nitric acid, drained, and dried. While several sources
claim that this recipe leads to a pigment of very good quality, the for-
mation of calcium sulphate, a scarcely soluble salt, from calcium hy-
pochlorite and sulfuric acid makes it unsuitable for the formation of pure
Prussian blue, as already discussed by Bersch at the beginning of the 20th century [22]. Alternatively, the use of calcium hypochlorite with only hydrochloric acid is reported for oxidation of the white precipitate [27,32,35–37]. Another commonly discussed recipe, by Gentele, relies on the addition of nitric and sulfuric acid to a boiling mixture containing the white precipitate [22,27]. It is then kept for 24 hours, washed with water, drained, and dried.

Other oxidation methods found in several sources include boiling the white precipitate with an iron(III) salt [27–29,32], the use of aqua regia [27,32], treatment with potassium dichromate and sulfuric acid [28,29,32,35,38], and the use of manganese(III) chloride [27–29,32]. The economy of these methods is often discussed, with the last two deemed too expensive, although it depends on the availability of the materials on a local scale. The use of an iron(III) salt, usually iron(III) sulphate, is the
Dyes and Pigments 225 (2024) 112093

S. Reus et al.

cheapest method, allowing for the reuse of the formed iron(II) salt for a new preparation of the white precipitate. While generally considered to lead to low-quality pigments, air oxidation is in fact sometimes reported as well [20–22,24,25,28,29].

3. Materials and methods

3.1. Chemicals and materials

All used chemicals were purchased from commercial suppliers and used without further purification. Potassium ferricyanide was obtained from Merck; iron(II) sulphate heptahydrate, potassium aluminium sulphate decahydrate and cold-pressed linseed oil were obtained from Sigma-Aldrich; nitric acid (65%) and hydrochloric acid (37%) were obtained from Honeywell Fluuka; magnesium sulphate heptahydrate was obtained from Acros Organics (now Thermo Scientific); blood meal was obtained from DCM, sold as a garden fertilizer; and citric acid was obtained from a local grocery store. All used water was deionised.

The pigment was washed three times, commonly through allowing the pigment to settle, followed by decantation and the addition of fresh water. Due to the small particle size and colloidal nature of Prussian blue, settling of the pigment can take a long time. Usually, the pigment was allowed to settle overnight, but in some cases multiple days or weeks were required for complete settling. In these instances, the mixture was centrifuged to facilitate completion of the three washing steps.

The difficulties in the purification of Prussian blue pigments, due to their small particle size and resulting long settling times, were already noted in the 19th century [28,29,35]. The pigments were then obtained after washing through filtration on a linen cloth, which was also not always a straightforward process, since some Prussian blue could initially pass through the filter cloth [27]. In such a case, the filtrate was collected until the filter was partially clogged with Prussian blue particles and the drops coming out of the cloth were no longer visibly blue, after which the collected filtrate was poured back onto the cloth. In this way, all blue particles were collected, and any loss of Prussian blue was minimised. After filtration, the pigment was obtained in a fluid paste consistency, containing a large amount of water. This paste was then wrapped in another linen cloth and pressed to remove most of the water. In some historical sources this process is described in more detail, and on a larger scale filter presses were used to press large amounts of pigment at the same time [27].

Here, the pigments were filtered on a small linen cloth after the three washing steps were completed (Fig. 3a). Subsequently, the pigment paste was pressed in the same linen cloth between two small wooden plates and using two screw clamps to tighten the press (Fig. 3b and c). The resulting very thick paste was then dried in an oven at 30–40 °C. This temperature was chosen based on temperatures specified in the studied historical sources. Some of them indicate that the drying temperature cannot be higher than 25–30 °C or should be in the range of 30–40 °C, while other sources give higher temperatures, up to 80 °C [27–29,32,35].

All of the replicated recipes as well as the followed purification steps for each recipe are given in more detail below. The original texts of all recipes, as well as further details on the corresponding historical sources can be found in the supplementary information.

3.2. General approach to studying sources and replicating recipes

Several historical sources from the mid-19th to early 20th century were studied, focusing on the period in which Vincent van Gogh was active as a painter. The studied sources include textbooks, treatises and encyclopaedias written by chemists, colourmen or apothecaries. The authors share their knowledge of natural sciences and clearly state that their overall intention was to educate the artist and the “practical man” [22] about the chemistry involved in artists’ materials.

For this paper, recipes for reproduction were selected according to a range of criteria. First of all, the frequency with which certain recipes were found in multiple sources was determined, since frequently reported methods may be indicative of common practices at the time (Table 1). Additionally, recipes explained in more detail, containing exact quantities of materials and exhaustive descriptions, were preferred. Recipes were also chosen in a way to cover the largest differences, while also taking into account the feasibility of performing these methods in a laboratory setting. Finally, the quality of the obtained pigment ascribed to the recipes was also taken into consideration.

In addition to following 19th and early 20th century recipes, Prussian blue pigments were also prepared according to the earliest known recipes for its preparation, from the 18th century. This allowed evaluation of how the preparation of Prussian blue changed over time and how this affected the pigment’s composition.

Once a blue product was obtained, several purification steps were followed, which were kept as similar as possible for all replicated recipes. The pigment was washed three times, commonly through allowing the pigment to settle, followed by decantation and the addition of fresh water. Due to the small particle size and colloidal nature of Prussian blue, settling of the pigment can take a long time. Usually, the pigment was allowed to settle overnight, but in some cases multiple days or weeks were required for complete settling. In these instances, the mixture was centrifuged to facilitate completion of the three washing steps.

The difficulties in the purification of Prussian blue pigments, due to their small particle size and resulting long settling times, were already noted in the 19th century [28,29,35]. The pigments were then obtained after washing through filtration on a linen cloth, which was also not always a straightforward process, since some Prussian blue could initially pass through the filter cloth [27]. In such a case, the filtrate was collected until the filter was partially clogged with Prussian blue particles and the drops coming out of the cloth were no longer visibly blue, after which the collected filtrate was poured back onto the cloth. In this way, all blue particles were collected, and any loss of Prussian blue was minimised. After filtration, the pigment was obtained in a fluid paste consistency, containing a large amount of water. This paste was then wrapped in another linen cloth and pressed to remove most of the water. In some historical sources this process is described in more detail, and on a larger scale filter presses were used to press large amounts of pigment at the same time [27].

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All of the replicated recipes as well as the followed purification steps for each recipe are given in more detail below. The original texts of all recipes, as well as further details on the corresponding historical sources can be found in the supplementary information.

3.2.1. Recipe A: a direct method for soluble Prussian blue, based on A. H. Church (1890)

A solution of potassium ferricyanide (2.15 g, 6.53 mmol) in water (16.3 mL) was added to a solution of iron(II) sulphate heptahydrate (3.62 g, 13.02 mmol) in water (16.3 mL) under constant stirring. A dark blue precipitate was immediately formed, and stirring was continued for two more minutes. Additional water (16.3 mL) was added, and the precipitate was left to settle for 24 h. The supernatant was decanted, and fresh water (16.3 mL) was added followed by thorough stirring. The precipitate was then left to settle, and the supernatant was decanted. The precipitate was washed a total of three times in this manner, was obtained via filtration on a linen cloth and was filter-pressed in the same cloth. Small samples were taken for analysis before and between each washing step. The pigments were dried in an oven at 30–40 °C.

![Fig. 5. XRD patterns of Prussian blue obtained using recipe A during different stages of the purification process. Peaks of several compounds are identified by symbols: * potassium ferricyanide, x potassium sulphate.](image-url)
3.2.2. Recipe B: an indirect method for soluble Prussian blue, based on J. Bersch (1893)

Sulfuric acid (95–98%, 1.60 mL) was added to a solution of iron(II) sulphate heptahydrate (1.77 g, 6.37 mmol) in water (19.7 mL). A solution of potassium ferrocyanide trihydrate (2.95 g, 6.98 mmol) in water (19.7 mL) was then slowly added under constant stirring. A pale blue precipitate was immediately formed. The mixture was heated to 60°C while nitric acid (65%, 2.91 mL) was added, turning the precipitate dark blue. After 40 min, no more darkening of the colour was observed, and the mixture was left to cool down. Water (20 mL) was added, and since no settling of the precipitate was observed after four days, centrifugation was used. The supernatant was decanted, and fresh water (40 mL) was added followed by thorough mixing. The mixture was centrifuged, and the supernatant was decanted. The precipitate was washed a total of three times in this manner. Small samples were taken for analysis before and between each washing step. Filtration on either a linen cloth or filter paper was found to be impossible due to the colloidal nature of the suspension, so instead the still-wet pigment obtained after the final decantation was dried in an oven at 30–40°C.

3.2.3. Recipe C: an indirect method for soluble Prussian blue, based on J. Bersch (1893)

Solutions of iron(II) sulphate heptahydrate (0.56 g, 2.01 mmol) in water (5.0 mL) and potassium ferrocyanide trihydrate (2.95 g, 6.98 mmol) in water (25 mL) were mixed under constant stirring. A pale blue precipitate was immediately formed. Sulfuric acid (95–98%, 0.23 mL) and nitric acid (65%, 0.75 mL) were added, and the mixture was heated to 60°C for 10 min, turning the precipitate dark blue. The mixture was left for four days to complete the oxidation, during which the precipitate settled. The supernatant was decanted, and fresh water (30 mL) was added followed by thorough stirring. The precipitate was then left to settle, and the supernatant was decanted. New water (30 mL) was added to repeat the washing in the same way, but centrifugation was found to be needed to separate the precipitate. The mixture was centrifuged, and the supernatant was decanted. The precipitate was washed two times in this manner, for a total of three washings. Small samples were taken for analysis before and between each washing step. Filtration on either a linen cloth or filter paper was found to be impossible due to the colloidal nature of the suspension, so instead the still-wet pigment obtained after the final decantation was dried in an oven at 30–40°C.
3.2.4. Recipe D: a direct method for soluble Prussian blue, based on J. Bersch (1893)

A solution of sodium sulphate was synthesised by mixing solutions of sodium bicarbonate (8.43 g, 100.35 mmol) in water (100 mL) and magnesium sulphate heptahydrate (12.37 g, 50.19 mmol) in water (30 mL) under heating at 90 °C. The formed insoluble magnesium carbonate was removed via filtration.

Saturated sodium sulphate solution (20 mL) was mixed with a solution of iron(III) chloride (1.31 g, 8.07 mmol) in water (13 mL). This mixture was slowly added to a solution of potassium ferrocyanide trihydrate (2.75 g, 6.51 mmol) in water (140 mL) under constant stirring. A dark blue precipitate immediately formed, and stirring was continued for ten more minutes. The precipitate was allowed to settle for 5 h, and the supernatant was decanted. Fresh water (170 mL) was added followed by thorough stirring, settling of the precipitate for one month, and decantation of the supernatant. New water (170 mL) was added to repeat the washing in the same way, but after one month no settling was observed. Small samples were taken for analysis before and between each washing step. The pigment was obtained via filtration on a linen cloth, followed by drying in an oven at 30–40 °C.

3.2.5. Recipe E: an 18th century method for Prussian blue, based on J. Woodward (1724)

Potassium carbonate (20 g) and finely crushed blood meal (20 g) were mixed in a porcelain crucible. The crucible was covered with a lid and heated in a furnace to 450 °C. This temperature was kept for about 90 min, after which it was increased to 650 °C for 10 min. The crucible was removed from the furnace and was emptied into boiling water (400 mL). The boiling was continued for 45 min, after which the mixture was filtered on a paper filter and washed with water (100 mL) three times. The combined filtrates were concentrated back to 300 mL.

Iron(II) sulphate heptahydrate (10 g) and potassium aluminium sulphate dodecahydrate (20 g) were dissolved in water (300 mL). This solution was slowly added to the still-hot “blood lye” solution. Immediately, a pale olive-green precipitate formed, with much effervescence. The precipitate was allowed to settle, and the supernatant was decanted, and fresh water (100 mL) was added. The mixture was stirred well, the precipitate was allowed to settle again, and the supernatant was decanted. Hydrochloric acid (37%, 15 mL) was slowly added to the precipitate, turning it dark blue. Water (100 mL) was added, and the mixture was stirred. The precipitate was allowed to settle, the supernatant was decanted, and fresh water (100 mL) was added, followed by thorough stirring. The precipitate was then left to settle, and the supernatant was decanted. The precipitate was washed a total of three times in this manner and was obtained via filtration on a linen cloth. Small samples were taken for analysis before and between each washing step. The pigments were dried in an oven at 30–40 °C.

3.2.6. Recipe F: an 18th century method for Prussian blue, based on R. Dossie (1758)

Potassium carbonate (10 g) and finely crushed blood meal (30 g) were mixed in a porcelain crucible. The crucible was covered with a lid and heated in a furnace to 450 °C. This temperature was kept for about 90 min, after which it was increased to 650 °C for 10 min. The crucible was removed from the furnace and was emptied into boiling water (400 mL). The boiling was continued for 45 min, after which the mixture was filtered on a paper filter and washed with water (100 mL) three times. The combined filtrates were concentrated back to 300 mL.

Iron(II) sulphate heptahydrate (10 g) and potassium aluminium sulphate dodecahydrate (20 g) were dissolved in water (300 mL). This solution was slowly added to the still-hot “blood lye” solution. Immediately, a pale olive-green precipitate formed, with much effervescence. The precipitate was allowed to settle, and the supernatant was decanted, and fresh water (100 mL) was added. The mixture was stirred well, the precipitate was allowed to settle again, and the supernatant was decanted. Hydrochloric acid (37%, 15 mL) was slowly added to the precipitate, turning it dark blue. Water (100 mL) was added, and the mixture was stirred. The precipitate was allowed to settle, the supernatant was decanted, and fresh water (100 mL) was added, followed by thorough stirring. The precipitate was then left to settle, and the supernatant was decanted. The precipitate was washed a total of three times in this manner and was obtained via filtration on a linen cloth. Small samples were taken for analysis before and between each washing step. The pigments were dried in an oven at 30–40 °C.

3.2.7. Recipe G: An ion exchange method for insoluble Prussian, based on A. H. Church (1890)

A solution of iron(III) chloride (0.51 g, 3.14 mmol) in water (20 mL) was added to a mixture of soluble Prussian blue (1.13 g, 3.68 mmol) in water (20 mL), under constant stirring. The mixture was heated to 90 °C and the stirring was continued for 40 min. The mixture was allowed to cool down, water (40 mL) was added, and the precipitate was left to settle. The supernatant was decanted, and fresh water (40 mL) was added, followed by thorough stirring. The precipitate was then left to settle, and the supernatant was decanted. The precipitate was washed a total of three times in this manner and was obtained via filtration on a linen cloth. Small samples were taken for analysis before and between each washing step. The pigments were dried in an oven at 30–40 °C.

3.3. Characterization

X-ray diffraction (XRD) patterns were recorded using a Bruker D8 Discover micro-diffractometer with a General Area Detector Diffraction System (GADDS) two-dimensional detector, using CuKα radiation (40 kV, 40 mA). Two-dimensional patterns were integrated using GADDS software and Bruker AXS Eva software was used for identification of individual components using the PDF database.

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were collected using a PerkinElmer Spectrum 100 FT-IR spectrometer equipped with a Specac Golden Gate single reflection diamond ATR. Spectra were obtained in a range of 4000–450 cm⁻¹ averaged over 16 scans.

The particle characteristics and elemental composition of the Prussian blues were investigated using scanning electron microscopy.
coupled with energy dispersive X-ray analysis (SEM-EDX) using a JEOL JSM-IT700HR, operated at 15 kV with a working distance of approximately 10 mm and secondary electron signal. The standardless ZAF quantification method was used for the semi-quantitative analysis of some samples.

3.4. Oil paint preparation

To be able to look into the colour of the prepared pigments when used in paints, oil paints were prepared by combining Prussian blue (0.03 g) and zinc white (0.60 g) in a 1:20 ratio with cold-pressed linseed oil (0.14 g). An automatic muller from Ault & Wiborg was used to mull the paints, until a suitable consistency and homogeneous colour was obtained. Paint films with a thickness of 200 μm on a polyester support were prepared using a drawdown bar, and small squares were painted out on commercial pre-primed canvas.

4. Results & discussion

Care must be taken when interpreting historical sources, since subjectiveness can play a large role. Several English translations of French and German books have been used, where the information may have changed between the source material and the translation. Certain common practices at the time may not be in use anymore, leading to differences in the way recipes were carried out then compared to how they are replicated now. For example, the starting materials were likely not available in a similar purity in the 19th and early 20th century compared to what is currently available. The purity of the starting materials is most often not discussed in the studied sources, although the presence of potassium sulphate as a contaminant in potassium ferrocyanide is sometimes mentioned [22,27]. In addition, not all sources provide detailed information regarding the amounts of materials used in synthesis, but rather use vague terms that may not be interpretable or
understandable to the contemporary reader. Still, it was possible to identify several common recipes found across the historical sources (Table 1). Most common are the indirect preparation of Prussian blue (recipes B & C), the direct preparation of so-called Turnbull’s blue from an iron(II) salt and potassium ferricyanide (recipe A), the preparation starting from nitrogenous animal matter (18th century recipes, E & F), and the direct preparation of soluble Prussian blue from an iron(III) salt and an excess of potassium ferrocyanide (recipe D). The addition of white compounds during the production of Prussian blue to give a cheaper kind of pigment is also commonly reported, but is not included here, since the focus is placed on pure Prussian blue pigments. The addition of zinc white upon preparation of the oil paints from the obtained Prussian blue pigments, as discussed in section 3.4, was not to replicate any specific recipe, but was required to be able to better visualise colour differences between the various pigments. Oil paints prepared containing only Prussian blue have an almost black appearance, making perception of colour differences much more difficult.

The selected recipes cover a wide range, including both indirect (B & C) and direct methods (A & D). The historical recipes replicated in recipes A and D specifically provide the preparation of soluble Prussian blue. The recipes of B and C merely describe the Prussian blue obtained as Chinese blue but based on the ratios of the starting materials used, these are also expected to lead to the formation of soluble Prussian blue. A process to convert soluble to insoluble Prussian blue was also replicated (G). The two 18th century recipes (E & F) can be classified as indirect methods as well, but not as soluble or insoluble, and will therefore be referred to as 18th century pigments.

4.1. Effects of washing, filtration and pressing of the pigment

As discussed in section 3.2, already in the 19th century it was noted that purification of Prussian blue pigment was difficult, both its washing and filtration, owing to the small particle size and colloidal nature [28, 29, 35]. Here, three different linen cloths were tested for their ability to be used as a filter as well as in a filter press, using recipe A. Whaleys’ Holland Linen Natural was found to let too much of the pigment pass through the filter, even when the filtrate was collected and poured back on the cloth several times. Whaleys’ Linen Greystone and the linen of unknown origin were found to be comparable in their performance and it was decided to perform all other purification steps using Whaleys’ Linen Greystone due to the known origin of this fabric.

The ATR-FTIR spectra obtained of the samples taken during the purification of Prussian blue obtained using recipe A are shown in Fig. 4. The absorption bands assigned to Prussian blue are the CN stretch mode around 2060 cm$^{-1}$, as well as the FeC stretch at 598 cm$^{-1}$ and the FeCN bending modes at 511 and 494 cm$^{-1}$ in the lower frequency region [39]. Additionally, several peaks corresponding to the presence of water can be found. Before any washing of the pigment, a single OH stretch vibration is found centred around 3200 cm$^{-1}$ and the bending mode is found as a relatively broad peak centred around 1655 cm$^{-1}$, both indicating bulk water with a strong hydrogen bond network [40]. Upon washing of the pigment, sharp peaks at 3630 cm$^{-1}$ and 1600 cm$^{-1}$ become visible. These can be attributed to, respectively, the OH stretch and bending modes of coordinated water minimally involved in hydrogen bonding, coordinated to the iron atoms of Prussian blue [40, 41]. Bulk water is also still present in the washed samples, indicated by its OH stretch mode found as a broad band centred around 3100 cm$^{-1}$.

After its initial synthesis and before washing, the presence of iron and potassium sulphates is observed through several bands between 1200 and 950 cm$^{-1}$ corresponding to sulphate stretching modes [42]. The antisymmetric bending mode of potassium sulphate is also clearly observed at 614 cm$^{-1}$. Iron(II) sulphate is used as starting material in
this synthesis, while potassium sulphate is formed as a by-product. The partial removal of these contaminants upon washing of the pigments and pressing of the pigment after filtration is clearly evidenced by a decrease in the intensity of these absorption bands.

In addition, upon washing of the pigment a significant shift of the CN stretch mode is observed to lower frequencies. While present at 2077 cm\(^{-1}\) in the unwashed sample, the band is found around 2050 cm\(^{-1}\) in the partly washed samples and at 2052 cm\(^{-1}\) in the final samples. Generally, the frequency of the CN stretch band depends on the electronegativity, oxidation state and coordination number of the metal it is coordinated to Ref. [42]. For iron(II) it will therefore be found at lower frequencies compared to iron(III). The observed shift to lower frequencies upon purification of the pigment therefore indicates the presence of more iron(II) and/or less iron(III), which may be associated with the removal of excess potassium ferricyanide from the pigment. A small peak corresponding to potassium ferricyanide was also found in the XRD patterns of the pigments before washing and pressing, at 28.9\(^\circ\) (Fig. 5). This peak is no longer visible after pressing of the pigment. The peaks corresponding to Prussian blue can also be found in the XRD patterns at 24.6\(^\circ\) (220), 35.3\(^\circ\) (400), 39.6\(^\circ\) (420), 43.6\(^\circ\) (422), 50.8\(^\circ\) (440), 54.2\(^\circ\) (600) and 57.2 (620). The performed SEM-EDX analysis provided no additional information.

4.2. Direct versus indirect synthesis

Fig. 6 shows the ATR-FTIR spectra of Prussian blue pigments obtained using the different replicated 19th century recipes and after complete purification. Notably, the two Prussian blue pigments prepared using indirect methods, B and C, show a CN stretch band at a slightly higher frequency, around 2060 cm\(^{-1}\) compared to around 2050 cm\(^{-1}\) for the pigments prepared according to the direct methods. This can be explained by a larger amount of potassium ferricyanide in the indirectly prepared pigments, as is also visible from the XRD patterns (Fig. 7). From the XRD patterns it can also be noted that the indirectly prepared pigment from recipe B shows less broad peaks, indicating a higher crystallinity of this compound.

Additional bands are present in the FTIR spectra of both indirectly prepared pigments, not observed for the directly prepared ones (Fig. 6). The band at 1378 cm\(^{-1}\) corresponds to the antisymmetric NO stretch vibration of nitrate ions and a small band at 825 cm\(^{-1}\) corresponds to the out-of-plane bending mode of nitrate ions [42]. The presence of these bands indicates the formation of potassium and/or iron nitrate due to the use of nitric acid for the oxidation step. The presence of potassium nitrate is confirmed by the XRD measurements (Fig. 7).

Additionally, the presence of potassium sulphate in the final pigment is also observed for the indirectly prepared Prussian blues, as well as the Prussian blue prepared using recipe D, as visible from the XRD patterns (Fig. 7) and from the antisymmetric bending mode observed as a small shoulder at 615 cm\(^{-1}\) in the FTIR spectra (Fig. 6). The pigment prepared according to recipe D, a direct synthesis of soluble Prussian blue from iron(III) chloride and potassium ferrocyanide in the presence of sodium sulphate, still contains various other contaminants as well, including potassium chloride and sodium chloride, as is clear from the XRD measurements (Fig. 7) and is further confirmed from the SEM-EDX results, where sulphur, chlorine and sodium were found. The presence of potassium sulphate was further confirmed using SEM-EDX mapping for the pigment prepared following recipe D, as well as those from the two indirect recipes, B and C (Figs. S1–S3).

The particle size of the Prussian blue pigments, investigated using SEM, does not vary greatly between the directly and indirectly prepared pigments (Fig. 8). The smallest still distinguishable particles (primary particles) for all of these pigments have sizes in the range of 20–30 nm. However, for pigments from recipes A, C and D, only few of these primary particles are clearly distinguishable, most of them having formed larger and irregularly shaped particles. Such larger particles are not observed in pigment B, where the primary particles are much more uniform in size, explaining the sharper peaks in the XRD pattern of this pigment (Fig. 7). Visually, the colour of the prepared oil paint is also very different for the recipe B pigment compared to the other three pigments, as seen in Fig. 9. The pigments from recipes A, C and D lead to oil paints with a duller shade and lower tinting strength. This may be explained by the fact that these pigments contain larger particles. Larger particles absorb less light compared to smaller particles, because they are not completely penetrated by the light, resulting in a lower tinting strength of the pigment. In contrast, the smaller primary particles of the recipe B pigment allow for more light absorption and a higher tinting strength, as is clearly visible from its oil paint in Fig. 9.

4.3. Conversion method

Recipe G involves boiling soluble Prussian blue, which was first prepared according to recipe A, with iron(III) chloride to convert it to insoluble Prussian blue. No significant differences are observed between the Prussian blue A starting material and the Prussian blue obtained from the conversion method in their ATR-FTIR spectra and XRD patterns (Figs. 10 and 11). However, chlorine was found to be present in pigment G through SEM-EDX analysis, indicating incomplete removal of chloride. SEM-EDX analysis also confirmed the presence of potassium, suggesting that the pigment contains potassium chloride or that the conversion of soluble to insoluble pigment was not or only partially successful. Semi-quantitative EDX analysis of both pigments shows that the relative amount of potassium has clearly decreased upon completion of the conversion recipe, as seen in Table 2. This suggests at least partial removal of potassium from the soluble Prussian blue.

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Table 2

Results of EDX analysis using standardless ZAF quantification method of soluble Prussian blue pigment (A) and its counterpart obtained through the conversion method (G).

<table>
<thead>
<tr>
<th>Element</th>
<th>Line</th>
<th>A, atom %</th>
<th>G, atom %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>K</td>
<td>35.75 ± 0.76</td>
<td>41.33 ± 0.77</td>
</tr>
<tr>
<td>N</td>
<td>K</td>
<td>37.73 ± 1.74</td>
<td>31.11 ± 1.53</td>
</tr>
<tr>
<td>O</td>
<td>K</td>
<td>8.91 ± 0.61</td>
<td>14.30 ± 0.71</td>
</tr>
<tr>
<td>S</td>
<td>K</td>
<td>0.96 ± 0.08</td>
<td>0.66 ± 0.06</td>
</tr>
<tr>
<td>Cl</td>
<td>K</td>
<td>–</td>
<td>0.33 ± 0.04</td>
</tr>
<tr>
<td>K</td>
<td>K</td>
<td>1.98 ± 0.12</td>
<td>0.56 ± 0.06</td>
</tr>
<tr>
<td>Fe</td>
<td>K</td>
<td>14.66 ± 0.49</td>
<td>11.70 ± 0.42</td>
</tr>
</tbody>
</table>
starting material through its replacement by iron(III) from the iron(III) chloride. A longer reaction time may allow for a final pigment containing even less potassium, but the lack of specific information in Church’s recipe, such as the exact amount of starting materials to be used and the required duration of the heating step, complicates accurate replication of his recipe. In contrast to what Church himself mentions in his recipe, it could also be possible that the Prussian blue prepared through this conversion process will simply always still contain some potassium. Due to the quick precipitation of Prussian blue, a certain amount of potassium is indeed always expected to be present, even when following recipes for the specific preparation of insoluble Prussian blue.

The high-magnification SEM image of the converted pigment shows a distinct change in the shape of the Prussian blue particles (Fig. 12). While the pigment particles of recipe A are irregularly shaped but mostly round, the primary particles in the recipe G pigment consist of clearly visible needle clusters. This may suggest that the replacement of potassium by iron(III) through the use of iron(III) chloride is a slow process, resulting in the formation of such clearly defined crystals. This highly specific shape of the pigment would allow for easy identification of a pigment prepared following the conversion method using SEM. The paints prepared from the recipe G pigment do not show a significant colour difference compared to the paint from recipe A (Fig. 9).

4.4. 19th versus 18th century recipes

The two pigments prepared according to the 18th century recipes of Woodward (E) and Dossie (F) still contain the starting material potassium aluminium sulphate hydrate after completion of the washing process, indicated by the OH stretch mode at 3345 cm\(^{-1}\) of water and the sulphate stretching vibrations around 1190, 1085 and 1055 cm\(^{-1}\) (Fig. 13) [43]. This is further confirmed by the SEM-EDX analysis, where aluminium is found to be present alongside potassium and sulphur.

Fig. 12. Scanning electron micrographs of the Prussian blue pigments prepared according to recipes A, G (conversion), E (18th century) and F (18th century). From left to right, the magnification of the micrographs increases and the scale bars are 50 μm, 1 μm and 200 nm. Some of the primary particles have been circled in the highest magnification micrographs for ease of visualisation.
Additionally, chloride and sometimes phosphorus were found in both pigments as well. The latter originates from the dried blood, while the former results from the use of hydrochloric acid in the synthesis, forming iron and/or potassium chlorides. Calcium sulphate was also identified using SEM-EDX analysis in the pigment from Dossie’s recipe (Fig. S4). Calcium also originates from the dried blood used as starting material, which was used in a relatively larger amount for Dossie’s recipe than for Woodward’s recipe.

In the FTIR spectra of the 18th century recipe pigments, a band at 1412 cm\(^{-1}\) is also present in both 18th century samples that cannot be found in the 19th century pigment. This band can be attributed to the bending vibration of an ammonium ion. The only source of ammonia can be the dried blood used in these 18th century recipes. It may have formed during the calcination of dried blood with potassium carbonate, resulting in the formation of ammonium carbonate, which is also clearly found to be present in the XRD pattern of the pigment prepared according to Woodward’s method (E, Fig. 14). A similar peak is not found for the pigment prepared according to Dossie’s method, which is likely related to the relatively smaller amount of potassium carbonate used in this recipe.

Scanning electron micrographs highlight a difference in particle size between the 18th and 19th century pigments (Fig. 12). Woodward’s recipe (E) results in primary particles of a fairly uniform size, but much larger than the 19th century pigment, 60–70 nm compared to 20–30 nm. Dossie’s recipe results in smaller particles, 30–40 nm, but much larger particles, about 300 nm in diameter, are also present. EDX analysis of these different-sized particles did not indicate any difference in elemental composition. When looking at the paints prepared from these pigments in Fig. 9, it is clear that the paint prepared from Woodward’s recipe pigment is lighter, indicating a lower tinting strength of the pigment, which can be caused by the larger particle size of this pigment. Alternatively, this pigment may still contain a larger amount of potassium aluminium sulphate, which was used in a relatively larger amount in Woodward’s recipe, compared to Dossie’s recipe.

4.5. Large-scale Prussian blue production in the 19th century

The recipes most commonly found in 19th century sources were replicated. Based on various comments in the sources, the most likely recipe for the commercial production of Prussian blue at the time can be further identified. While the preparation of a soluble Prussian blue from an iron(III) salt and an excess of potassium ferrocyanide is often reported, here replicated in recipe D, some sources also indicate the inferiority of soluble pigments, making it less likely that this recipe was used on a commercial scale [22, 35–37]. In contrast, the indirect methods (recipes B and C) and direct method for so-called Turnbull’s blue, starting from an iron(II) salt and potassium ferricyanide, (recipe A) are said to result in the highest quality pigment in terms of intensity and colour. However, when preparing oil paints out of these pigments, only a significant difference in the properties of the pigment prepared following recipe B was found, having a higher tinting strength and less dull shade. The suggested higher quality colour of pigments from recipes A, B and C compared to recipe D could therefore not be confirmed. Still, in the 19th century it was evidently believed that such recipes did lead to a better-quality pigment. The higher cost of potassium ferricyanide at the time makes the direct method for Turnbull’s blue less economical than the indirect methods. Therefore, the indirect methods for the preparation of Prussian blue seem most likely to have been used on a larger scale in the 19th century, which is in line with this type of method still being in use today for the production of commercial Prussian blue.
A wide range of oxidation methods used in the direct method are reported in the 19th and early 20th centuries, with little note on their effect on the quality of the produced Prussian blue. Most commonly, it is discussed that the decision on which oxidation method to use depends on the cost of the required materials and may be different depending on local circumstances. It is therefore difficult to point to one oxidation method as having been most likely used for the commercial production of Prussian blue in the 19th century. However, as is also evident from the analysis of the pigments obtained from the replicated recipes, the presence of certain contaminants may tell us what kind of oxidation method was used. For example, the presence of nitrates may point to the use of nitric acid, while the presence of calcium sulphate may point to the use of Hochstätter’s oxidation method, not replicated here but discussed in section 2.2.

5. Conclusion

Various historical sources from the 19th and early 20th centuries containing recipes for the production of Prussian blue were studied. Most prevalent across all sources were the indirect production of Prussian blue from an iron(II) salt and potassium ferrocyanide, followed by an oxidation step, the direct production of so-called Turnbull’s blue from an iron(II) salt and potassium ferricyanide, the production of Prussian blue starting from nitrogenous animal matter, and the direct production of soluble Prussian blue from iron(III) salt and an excess of potassium ferricyanide. Based on comments regarding the quality of the Prussian blue pigments obtained and the costs of the recipes, the indirect recipes seem most likely to have been used for the production of commercial Prussian blue, but recipes of all four types were replicated.

Differences between the pigments prepared according to various recipes were mainly found in the presence of certain contaminants, often potassium ferricyanide and potassium sulphate, but several contaminants specifically related to the replicated recipe could also be identified. If present in historical paints or pigments, such contaminants may give insight into the preparation method used. Several differences in particle size and shape between the different pigments were also identified, resulting in different shades and tinting strengths of the pigment and oil paints prepared from them. A more detailed investigation into the influence of the contaminants and particle characteristics on the properties of Prussian blue used in oil paints, and on any of the unexplained degradation phenomena in Prussian blue paint strokes will have to be conducted in the future.

CRediT authorship contribution statement

Suzanne Reus: Writing – original draft, Visualization, Supervision, Methodology, Investigation, Data curation, Conceptualization. Elena de Sotto Bastos: Methodology, Investigation, Data curation. Maarten R. van Bommel: Writing – review & editing, Supervision, Methodology, Funding acquisition, Conceptualization. Klaas Jan van den Berg: Writing – review & editing, Supervision, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2024.112093.

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