

## THE EARLY USE OF PRUSSIAN BLUE IN PAINTINGS

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### ABSTRACT

*As far as is known, the pigment Prussian blue was synthesised for the first time in Berlin in the early 1700s. It is commonly assumed that the pigment was not used in paintings before the 1720s. The presence or absence of this pigment is often used to answer questions concerning the dating and authenticity of art objects from the 18th Century.*

*For the very first time, a large collection of French 18th Century paintings by Antoine Watteau (1684-1721) and his circle has been studied in detail. The pigments of more than fifty paintings from the collection of Frederick II of Prussia have been analysed with non-destructive methods using a complementary combination of micro X-ray fluorescence analysis, optical microscopy and spectroscopy in reflection mode.*

*Most interesting in this context is evidence of Prussian blue in two earlier works by Watteau from about 1710. It shows that Prussian blue must have found its way from Berlin to Paris by around 1710 at the latest.*

*In the search for further proof that Prussian blue was used in paintings dating back to the same years, we also analysed blue pigments in works by painters of the Prussian court, and of other European courts. The court painters were closely connected to the Royal Academy of Arts in Berlin, where the pigment was available no later than 1709.*

*This investigation shows that Prussian blue was used by painters at the Prussian court, in Rotterdam, and Paris much earlier than previously assumed. It was already used in 1710, and this to a surprisingly large extent. To date, the painting "Entombment of Christ", dated 1709 by Pieter van der Werff (Picture Gallery, Sanssouci, Potsdam) is the oldest known painting where Prussian blue has been used.*

*Historical sources and the material findings mentioned above date the first synthesis of the pigment by Johann Jacob Diesbach in Berlin to about 1706.*

### INTRODUCTION

The Prussian Palaces and Gardens Foundation Berlin-Brandenburg in Potsdam, Germany, is presently preparing a catalogue of its collection of French 18th-century paintings collected by Frederick II of Prussia (1712-1786) [catalogue]. Works by Antoine Watteau (1684-1721), Nicolas Lancret (1690-1743), and Jean-Baptiste Pater (1695-1736) feature prominently in this collection. A team of art historians, restorers and scientists is currently investigating more than 50 paintings. For the first time, one of the largest collections of its kind is being studied in-depth.

This study shows that the pigment Prussian blue, an iron hexacyanoferrate complex compound, was used by the painters in Paris much earlier than has been previously assumed [Bartoll et al.]. Most surprising was the evidence of Prussian blue in two earlier paintings by Watteau: "La mariée de village" (SPSG, Potsdam, Sanssouci Palace, see Figure 1) and "Embarkation to Cythera" (Städel Museum, Frankfurt). Both paintings are conventionally dated to around 1710.

Prussian blue was synthesised for the first time in Berlin in the early 1700s. Most literature on pigment history assumes that Prussian blue was rarely or not used by painters before the 1720s. Harley wrote in this context: "...one might expect the pigment to have been acclaimed

immediately by artists, but such was not the case." and "...it appears to have been well established by the middle of the eighteenth century..." [Harley]. Assuming the stylistic dating of the paintings is correct, this means that Prussian blue must have found its way from Berlin to Paris by around 1710 at the latest.



*Figure 1: A. Watteau, "La mariée de village" (SPSG, Sanssouci Palace, Inv. No. GK I 5603, photo: W. Pfaunder) Watteau painted the sky and figures with ultramarine, and an underlayer containing Prussian blue.*

The question of the early use of Prussian blue is of some importance, because the presence or absence of the pigment in art objects is frequently used for their relative dating, and to answer questions concerning authenticity. This work aims to clarify some misunderstandings concerning the first production and use of Prussian blue in paintings. In order to do this, historical sources were studied and a number of paintings were analysed in search of new material findings.

### **APPROACH OF PIGMENT ANALYSIS**

The search for Prussian blue in paintings of the beginning of the 18th Century can be rather difficult. This holds especially true for Watteau, as many of his paintings have undergone several conservation and restoration campaigns, often dating back to as early as the 18th Century. This makes not only the analysis of pigments difficult; there is also the risk of confusing original with later ingredients. The Prussian blue applied by the artists reacts sensitively to light. In some paintings it has strongly faded, or has changed into a grey colour.

A basic principle of this investigation was to take no samples from the visible areas of the paintings. The pigments were studied with non-destructive methods, using a complementary combination of optical microscopy, micro X-ray fluorescence analysis and optical spectroscopy in reflection mode [Bartoll et al.]. In a few cases, samples were taken from paint layers from the outer edges or tacking margins of the painting, in order to produce cross sections, and to carry out infrared spectroscopy.

The X-ray fluorescence (XRF) measurements were performed using the mobile energy-dispersive X-ray fluorescence spectrometer "ARTAX" (Bruker AXS Microanalysis GmbH, Berlin, Germany) [Bronk et al.]. The use of open helium purging equipment for the excitation and detection paths enabled the detection of all elements down to sodium. All spectra were measured using a voltage of 45 kV, and a current of 600  $\mu$ A for the excitation.

Once XRF ruled out the occurrence of copper and cobalt, only Prussian blue, ultramarine and indigo could possibly represent blue pigments in paintings from this period. All three of these pigments, however, cannot be distinguished with certainty by XRF. Indigo is not "visible" to XRF at all because of its organic nature. In theory, when using XRF, Prussian blue might be identified by its iron content, and ultramarine by the occurrence of sodium, sulphur, silicon and aluminium. Due to the shielding effect of the varnishing layers, sodium and sulphur could hardly be detected - both elements have a relatively low energetic fluorescence radiation. Like iron, both silicon, and, to a lower extent, aluminium - all present in the ground layers as part of the ochre - were detected in almost all of the measurements. Additional measures had to be taken into account in order to distinguish between the three pigments.

The shape and size of the pigment grains were observed directly on the paintings using an optical microscope (Carl Zeiss OPMI1-FC; magnification up to 50x). Ultramarine appears in rather large particles through the optical microscope. Prussian blue and indigo are fine powders (grain size < 1  $\mu\text{m}$ ). Thus, when observing the surface of the painting through the microscope, only a blue coloured matrix should ideally be visible for the latter two pigments. The powder particles, however, often stick together and for this reason, they cannot always be distinguished from mineral pigments with certainty using this method.

Thus, a third non-destructive method was applied: optical spectroscopy in reflection mode [Johnston-Feller]. This was performed using a CM-2600d Spectrophotometer (Minolta, Japan) equipped with pulsed xenon light sources, an integrating sphere, and a silicon photodiode array detector. The measurement spot size was 3 mm in diameter. Spectra were recorded in reflection mode at a range of 360 nm to 740 nm, with a step size of 10 nm. They were compared to those of positively identified pigments in original paintings. Figure 2 shows optical reflection spectra of blue pigments measured directly on the original paintings. As can be seen, the spectra differ significantly. The spectra of ultramarine and indigo show a strong reflection in the red range above 650 nm. Prussian blue does not have this red component.

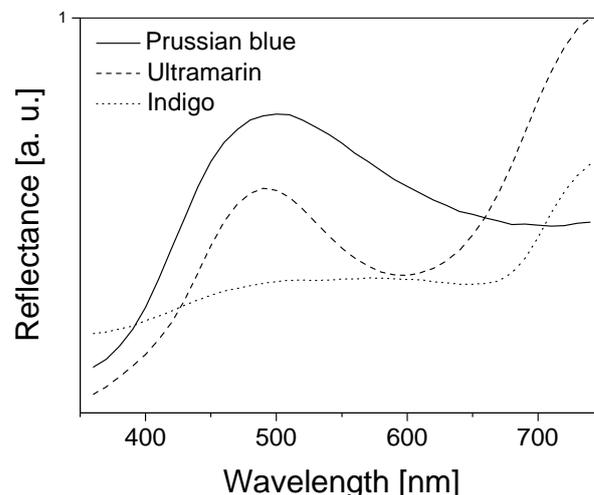


Figure 2: Optical reflection spectra of blue pigments measured directly on paintings

A Chelsea filter was very helpful to pre-select paintings or appropriate blue areas in paintings for analysis [Bartoll]. Areas illuminated by light passing through the filter remain dark blue in the case of Prussian blue, and reddish in the case of ultramarine and indigo. The red component in the reflection spectrum mentioned above is responsible for this effect in regard to the latter two pigments.

Cross sections were investigated by microscopy using visible and UV light (Leica DMLM microscope), and some by electron microscopy (REM-EDX, Hitachi S-2700).

A paragon 1000PC FTIR spectrometer (Perkin Elmer), in combination with an i-series FTIR microscope (Perkin Elmer), was used for infrared spectroscopy in transmission mode. Samples were pressed on a diamond. The IR spectrum of Prussian blue shows a characteristic band at  $2083\text{ cm}^{-1}$  due to the C-N stretch vibration [Berrie].

### **EARLY PRUSSIAN BLUE - HISTORICAL SOURCES**

Prussian blue is first mentioned in a letter written by Johann Leonhard Frisch (1666-1743) to the president of the Royal Academy of Sciences, Gottfried Wilhelm Leibniz (1646-1716), from March 31, 1708 [Frisch]. The pigment was also an important topic in other letters of their correspondence between 1708 and 1716. By August 1709, the pigment had been termed "Preussisch blau"; by November 1709, the German name "Berlinisch Blau" had been used for the first time [Frisch].

Although Frisch was not the inventor of the pigment, he could be considered to be someone we would today call a product manager. He claimed to have improved the pigment, e.g. by means of an acid treatment [Frisch]. He was very active in promoting and selling the pigment. Frisch himself is the author of the first known publication of Prussian blue in the paper "Notitia Coerulei Berolinensis nuper inventi" in 1710 [Frisch 1710], as can be deduced from his letters [Bartoll et al.]. The publication gives information on the availability of the pigment at the booksellers of the Royal Academy of Sciences in Berlin.

Three historical sources mention Diesbach as the actual inventor of the pigment [Frisch; Stahl; Berger]. Diesbach had been working for Frisch since about 1701 [Frisch]. There is much confusion in literature about Diesbach's first name. Most historical sources do not mention a first name at all. Only Berger refers to him as Johann Jacob Diesbach [Berger].

In 1731, Stahl published a story dealing with the incidence of the first synthesis of Prussian blue [Stahl]. The story involves not only Diesbach but also Johann Conrad Dippel. No other known historical source mentions Dippel in this context. It is therefore difficult to judge the reliability of this story today.

There is also much confusion regarding the date of the discovery. Textbooks and encyclopaedia often give the year as 1704 in this context. However, they fail to give the source of this date. Harley suggests a conjectured date for the discovery between 1704 and 1707, as this was the period when Dippel was living in Berlin [Harley]. Frisch wrote in his letter from March 31, 1708, that he had already made some money with the pigment [Frisch]. This suggests that the discovery must have taken place some time before 1708. The pigment, however, is not mentioned in his letters to Leibniz from 1706 and 1707. It seems to be feasible that this period in time includes the day of discovery and the process of a secret experimentation in order to develop a market-ready product. According to Berger, Prussian blue was developed by Diesbach in 1706 [Berger; Brather]. All in all, it seems that Prussian blue was synthesised for the first time around 1706 by Johann Jacob Diesbach in Berlin.

Not later than 1709, Frisch and also Joseph Werner, the director of the Royal Academy of Arts in Berlin, began sending samples of Prussian blue to a number of painters across Europe [Frisch]. Wolfenbüttel, Leipzig, Basel, Paris and Italy are all mentioned in this context.

According to the letter from July 26, 1715, it was probably in 1714 that Frisch sent 100 pounds of the pigment to Paris (1 pound = 30 thaler). In 1716, the pigment was known in Petersburg and Armenia [Frisch]. A historical source gives evidence of the purchase of Prussian blue by the monastery church of Melk in Austria in 1716 [Koller]. The pigment is mentioned in the 1721 edition of the book "der wol anführende Mahler" by Cröker [Cröker]. In 1724, the recipe was finally published by Woodward [Woodward].

Considering the historical sources mentioned above, Prussian blue cannot be expected to be found in paintings created before 1706. It is also not very likely to be found in art objects produced before 1708. It might, however, appear as a blue pigment all over Europe from 1708 onwards. How are these statements reflected in material findings?

### **EARLY PRUSSIAN BLUE - MATERIAL FINDINGS**

Watteau, Adrian van der Werff (1659-1722), and Giovanni Antonio Canal (Canaletto) (1697-1768), are frequently mentioned in literature as the first painters to have used Prussian blue in easel painting [Berrie]. However, the earliest works by Canaletto containing Prussian blue date back to the time between 1719 and 1723, which is rather late in this context. More recently, evidence of Prussian blue was found in paintings by the Austrian artists Jacopo Zanussi, Johann Georg Schmidts, and Franz von Tamm from 1715 [Richard et al.]. The pigment was also found in a painting by the Dutch painter Matthys Naiveau again from 1715 [Groen]. Traces of Prussian blue may be present on the decorated fencing from 1712/13 at Charlottenburg Palace, Berlin [Becker].

The investigations presented here concentrate on Paris (Watteau and his circle), Düsseldorf / Rotterdam (van der Werff brothers), and, last but not least, on Prussia as the place of origin.

#### **Paris: Pater, Lancret, Watteau**

The paintings by Pater of the Prussian collection date back to around 1728 to 1736 [catalogue]. Prussian blue was the only blue pigment detected in all twenty-five paintings investigated here [Bartoll et al.]. Even green colours are all a mix of Prussian blue and Naples yellow.

Thirteen of the eighteen paintings by Lancret investigated here contain Prussian blue. Lancret produced these works between about 1719 and 1743 [catalogue]. In his earlier works, he still used more ultramarin, whereas his later works are increasingly dominated by Prussian blue. Most typical of this artist is his use of ultramarin for the sky and Prussian blue for the figures. He used mixed greens with Prussian blue in addition to green earth pigments [Bartoll et al.].

It is assumed that Prussian blue was used in the painting "Comédiens italiens", National Gallery of Art, Washington (D. C.) [Fisher]. However, the painting might only be a copy after Watteau [Börsch-Supan 2000]. The thirteen paintings by Watteau investigated here date back to about 1709 to 1721. Prussian blue was identified in five of them [catalogue]. These are: "Recréation italienne" (Sanssouci Palace, Potsdam; see also [Becker]), "La mariée de village" (Sanssouci Palace, Potsdam), as well as the Italian and the French comedies (both Gemäldegalerie Berlin, SPK). His work, the "Embarkation to Cythera", today in the Städel Museum, Frankfurt, Germany, also very likely contains the pigment (optical spectroscopy and microscopy SPSG; REM-EDX by M. Eveno, C2RMF, Louvre, Paris). Watteau used Prussian blue in these paintings in combination with ultramarin. Greens mixed with Prussian blue were not identified in the case of Watteau.

"La mariée de village" and the "Embarkation to Cythera" represent earlier works by Watteau. Both paintings are conventionally dated to around 1710. This proves that Watteau already used Prussian blue in his earlier works. Assuming that the stylistic dating of the paintings is correct, this means that Prussian blue must have found its way from Berlin to Paris in around 1710. As mentioned above, Frisch sent a large amount of Prussian blue to Paris around 1714. However, he may have sent some smaller quantities long before this date.

### **Düsseldorf / Rotterdam: Van der Werff Brothers**

Apart from Frisch, Dippel, who went to Holland in 1707 [Ackermann], or Dutch members of the Prussian academy such as van Royen might have had the opportunity to introduce the pigment to painters in Holland. It is interesting in this context to follow the path of the van der Werff brothers Adrian and Pieter. They worked in Düsseldorf and Rotterdam. The painting "Jacob blessing the sons of Joseph" (Allen Memorial Art Museum, Oberlin) is the always mentioned in literature as proof of Adrian van der Werff's use of Prussian blue. Recent studies, however, have revealed that this painting was not finished by van der Werff himself, but by Henrik van Limborch in 1728 [Gaetgens; Jansen]. Therefore, Limborch might have been the one who used Prussian blue at a time when it was already very common.

Sixteen paintings by Adrian van der Werff dating from 1705 to 1714 (collection of Bayerische Staatsgemäldesammlung, Munich, and SPSPG) were analysed in cooperation with the Doerner Institute, Munich, Germany. No Prussian blue could be identified in these paintings. Therefore, it appears that Adrian van der Werff was likely not among the first artists to use the pigment.

However, Prussian blue could be identified in the painting "Entombment of Christ" (Picture Gallery, Potsdam, see figure 3) by Pieter van der Werff. The painting is signed "P van der Werff", and is dated 1709. Prussian blue is used in the sky, and in Mary's veil. This painting represents the earliest known proof to date of the use of this pigment in a painting.



*Figure 3: Pieter van der Werff, "Entombment of Christ" (Picture Gallery, Sanssouci, Inv. No. GK I 10008)*

### **Berlin / Potsdam: The Prussian Court Painters**

The court painters were closely connected to the Royal Academy of Arts in Berlin, where Prussian blue was available not later than 1709. This academy was located in the same building as the Academy of Sciences, where the pigment was known not later than 1708 [Frisch]. It therefore seems likely that the court painters could have been involved in the first use and spreading of this pigment.

Prussian blue was identified in twelve paintings (Sanssouci Palace, Potsdam; Charlottenburg Palace, Berlin) by Antoine Pesne (1683-1757) that date between 1710 and 1715 [Bartoll et al.]. Among these are the portraits of Théodore Giou de Briou (Inv. No. GK I 881) and Philip William of Brandenburg-Schwedt (Inv. No. GK I 7346) from about 1710 [Börsch-Supan 1986]. Pesne was born in Paris, educated in France and Italy, came to Berlin in 1710, and took the position of court painter of Frederick I of Prussia.

Prussian blue was also detected in the portraits of Frederick I of Prussia (Inv. No. GK I 50478, New Palace, Potsdam, dated 1713) by Samuel Theodor Gericke (1665-1730) and of Freifrau von Blaspiel (Inv. No. GK I 3295, Charlottenburg Palace, Berlin, c 1710-12 [Baumbach and Bischoff]) by Adam Manyóki (1673-1757), in the "Paradise bird" (Inv. No. GK I 30225, Grunewald Hunting Lodge, Berlin, dated 1711) by Wilhelm Frederik van Royen (1645-1723), and in at least four paintings by Friedrich Wilhelm Weidemann (1668-1750). This means that Prussian blue was used by painters at the Prussian court in important paintings shortly after its invention.

### **CONCLUSIONS**

Prussian blue was probably synthesised for the first time by Johann Jacob Diesbach in Berlin around the year 1706. Shortly after, not later than 1708, Johann Leonhard Frisch began to promote and sell the pigment across Europe. The pigment was first named "Preussisch Blau", and later, in November 1709, the name was changed to "Berlinisch Blau". The pigment was accepted by artists much earlier than previously assumed, as can be proven on the basis of a number of examples. To date, the painting "Entombment of Christ" (Picture Gallery, Sanssouci, Potsdam, dated 1709) by Pieter van der Werff is the oldest known painting that makes use of Prussian blue. Around 1710, painters at the Prussian court such as Pesne, Gericke, Manyóki, and Weidemann were already using the pigment to a surprisingly large extent. At around the same time, Prussian blue arrived in Paris, where Watteau and later his successors Lancret and Pater used it in their paintings.

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