ON THE DISCOVERY AND HISTORY OF PRUSSIAN BLUE

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Introduction

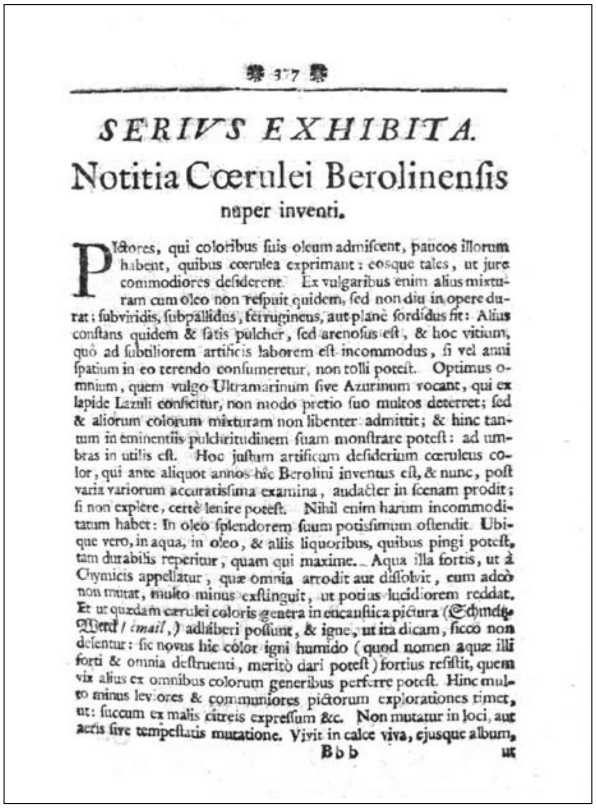
In the early 18th century Prussian Blue (ferric hexacyanoferrate(II)), the first purely synthetic pigment, was discovered. This new blue pigment was less expensive and more readily available or more easily produced as compared to ultramarine or other blue pigments which were in use at the time as a blue color in paintings. Prussian Blue is a very stable compound with the exception of being labile in alkaline media. The discovery of Prussian Blue is still enigmatic and has not been well researched. Today, Prussian Blue is still used as a pigment, but it also has other applications ranging from electrochromics and sensors to poison antidotes.

The Conventional Story of the Discovery of Prussian Blue

Prussian Blue was first mentioned in the scientific literature in the first issue of the publication of the Royal Prussian Society of Sciences (Königlich Preussische Sozietät der Wissenschaften) (1) *The Miscellanea Berolinensia ad incrementum Scientiarum* in 1710 (2). (A German translation of this Latin text was subsequently published (3)). This first written account of Prussian Blue was published anonymously (the author was most probably Johann Leonhard Frisch as will be discussed below). This early report revealed almost nothing of the discovery of Prussian Blue nor did it give a method for the preparation of the pigment. Rather, it was a kind of advertisement for the new material under the auspices of the new scientific society, and it was stated that Prussian Blue could be bought from the book dealers of the society.

The conventional story of the invention of Prussian Blue was told by Georg Ernst Stahl (1660-1734) (4) in a book he published in 1731 (5). In this book, published about 25 years after the discovery of Prussian Blue, Stahl reported 300 experiments supporting the phlogiston theory of oxidation and combustion. As related by Stahl (5), the discovery of Prussian Blue (Stahl writes "Caeruleum Berolinense") took place in Berlin in the laboratory of Dippel ("Dippelius"), although no date was given. Dippel was preparing so-called animal oil ("oleum animale") by distillation of animal blood to which potash (potassium carbonate, or as Stahl writes "Sale tartari") was added. Concurrently, a color maker named Diesbach was working in Dippel's laboratory. Diesbach was attempting to produce Florentine lake, a red pigment based on cochineal red. Usually he did this by precipitation of an extract of chochineal (produced by boiling dried cochineal insects with water to extract the carminic acid) with alum ($KAl(SO_4)_2 \cdot 12H_2O$), iron sulfate ("Vitrioli Martialis"), and potash ("Sale alcalico Tartari"). However, having no more potash, he borrowed some from Dippel that had been used in his animal oil production. This potash was contaminated with hexacyanoferrate; and therefore the addition of contaminated potash to the solution, which already contained iron sulfate, resulted in a blue precipitate, the Prussian Blue, instead of the expected red product.

To date, these two reports (2, 5) have been considered to be the only sources of information on the very early history of Prussian Blue. However, there exists a neglected source of information on the first years of Prussian Blue: the correspondence of Leibniz.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SERIVS EXHIBITA.

Notitia Cœrulei Berolinenſis nuper inventi.

Pictores, qui coloribus ſuis oleum admiſcent, paucos illorum habent, quibus cœrulea exprimant: eosque tales, ut jure commodiores deſiderent. Ex vulgaribus enim alius mixturam cum oleo non reſpuit quidem, ſed non diu in opere durat; ſubviridis, ſubpallidus, ferrugineus, aut planè ſordidus fit: Alius conſtans quidem & ſatis pulcher, ſed arenoſus eſt, & hoc vitium, quô ad ſubtiliorem artificis laborem eſt incommodus, ſi vel anni ſpatium in eo terendo conſumeretur, non tolli poteſt. Optimus omnium, quem vulgo Ultramarinum ſive Azurinum vocant, qui ex lapide Lazuli conficitur, non modo pretio ſuo multos deterret; ſed & aliorum colorum mixturam non libenter admittit; & hinc tantum in eminentiis pulchritudinem ſuam monſtrare poteſt: ad umbras inutilis eſt. Hoc juſtum artificum deſiderium cœruleus color, qui ante aliquot annos hic Berolini inventus eſt, & nunc, poſt varia variorum accuratiſſima examina, audacter in ſcenam prodit; ſi non explere, certè lenire poteſt. Nihil enim harum incommoditatum habet: In oleo ſplendorem ſuum potiſſimum oſtendit. Ubique vero, in aqua, in oleo, & aliis liquoribus, quibus pingi poteſt, tam durabilis reperitur, quam qui maxime. Aqua illa fortis, ut à Chymicis appellatur, quæ omnia arrodit aut diſſolvit, eum adeò non mutat, multo minus exſtinguit, ut potius lucidiorem reddat. Et ut quædam cærulei coloris genera in encauſtica pictura (Schmeltz-Werck / email,) adhiberi poſſunt, & igne, ut ita dicam, ſicco non delentur: ſic novus hic color igni humido (quod nomen aquæ illi forti & omnia deſtruenti, meritò dari poteſt) fortius reſiſtit, quem vix alius ex omnibus colorum generibus perferre poteſt. Hinc multo minus leviores & communiores pictorum explorationes timet, ut: ſuccum ex malis citreis expreſſum &c. Non mutatur in loci, aut aeris ſive tempeſtatis mutatione. Vivit in calce viva, ejusque album,

Bbb ut

***Figure**. First page of the first publication on Prussian Blue from the Miscellanea Berolinensia ad incrementum Scientiarum (2)*

The Correspondence of Leibniz

Gottfried Wilhelm Leibniz corresponded with an enormous network of people scattered throughout Europe. This correspondence was conducted in several languages, mainly in Latin, French, and German (6).

A major additional source on the very early history of Prussian Blue is a set of letters sent from Johann Leonhard Frisch (1666-1743) in Berlin to Gottfried Wilhelm Leibniz in Hannover (7), which were first published in a book in 1896 (8). This book contained 37 letters from Frisch to Leibniz between the end of 1706 and September 19, 1716 (Leibniz died on November 14, 1716), together with three responses from Leibniz to Frisch. Thirteen of these letters from Frisch mention the new pigment Prussian Blue; and in five letters Diesbach, one of two inventors indicated by Stahl (5), is mentioned (Frisch writes his name "Diessbach" or "Dieszbach"). Diesbach is mentioned in direct connection with the new blue color. The letters do not state the first name of Diesbach, the story of the invention of Prussian Blue, or the names of the inventors.

Johann Leonhard Frisch had been living in Berlin since 1698. He taught at the Berlin Gymnasium located in the former Grey Monastery of the Franciscans. Frisch had been a member of the Berlin Society of Sciences since 1706 (8). In his first letter to Leibniz in which Prussian Blue is mentioned, written on March 31, 1708, Frisch informed Leibniz that he had already earned some money with his blue color. In the second letter that mentions Prussian Blue, dated April 28, 1708, Frisch stated that he had made the color better than the original inventor had done and that the production process was now less expensive.

In a much later letter of September 14, 1715, however, Frisch informed Leibniz that he himself was the inventor. This statement may have been a reaction to an assertion made to Leibniz by Diesbach's father-in-law Müller (at this time residing in Vienna), who claimed to be the inventor of Prussian Blue. This letter also clarified that the secret of the production of Prussian Blue was strongly protected and that at this time (in 1715), at least in Berlin, only Diesbach and Frisch knew how to make Prussian Blue. (The name of Dippel, the second possible original inventor, did not appear in the letters from Frisch to Leibniz).

The name Prussian Blue ("Preussisch-blau") is used in one letter dated August 25, 1709 and the name Berlin Blue ("Berlinisch Blau" or "Berlin Blau") in two later letters (from November 9, 1709 and September 2, 1712). However, in most letters, it was simply called the blue color ("blaue Farb(e)"). The name of Diesbach appears for the first time in a letter from September 28, 1709, which stated that Diesbach had printed an informational sheet for painters about the blue color.

Diesbach seems to have been active in alchemical studies as well. Indications of these investigations appeared in two letters (from September 28, 1709 and undated, but perhaps from about spring 1710).

In a letter of November 9, 1709, Frisch sent Leibniz a Latin text about the blue color. In another letter from January 30, 1710, he told Leibniz that the text *"notitia* *caerulei Berolinensis"* that Leibniz sent back had been added to the texts for the *Miscellanea*. These two letters most probably refer to the first publication on Prussian Blue (2). It appears that Frisch was the author of this publication which had been published anonymously.

The profitable business of selling Prussian Blue was cause to protect the secret of its preparation. In several letters to Leibniz Frisch revealed details of his commercial success with selling Prussian Blue. At that time, Diesbach was producing Prussian Blue while Frisch was selling it, at least outside Berlin. In a letter dated October 29, 1712, Frisch wrote that he was not able to satisfy the demand for Prussian Blue. Soon imitation Prussian Blue, perhaps indigo blue being sold as Prussian Blue, appeared on the market (letter from August 25, 1709).

Because of the large amount of money Frisch earned by selling Prussian Blue, he was able to buy land outside the Spandau Gate of Berlin. He used this land for his botanical experiments with mulberry trees and other plants, according to a letter from July 26, 1715. As an example of his sales, this letter indicated that he sold 100 pounds of Prussian Blue in Paris for 30 thaler per pound in the year 1714.

Sales of Prussian Blue that were explicitly described included those to Wolffenbüttel (9) (letters from September 28, 1709 and November 9, 1709), in Paris (letters from July 26, 1715 and September 19, 1716) and in St. Petersburg (letter from September 19, 1716). In the last of these letters, Frisch reported to Leibniz that in Paris two factories that produced ultramarine (10) ("Outremer") had been closed because of the large amounts of Prussian Blue he delivered to Paris.

Leibniz was obviously somewhat involved in the sale of Prussian Blue or at least was active in informing potential customers about this new pigment. Frisch wrote Leibniz in a letter dated September 2, 1712, that Bernoulli (a Swiss mathematician from Basel who corresponded with Leibniz, see below) could purchase his half pound of Prussian Blue in Leipzig from Gleditsch for 15 thaler.

The only use of Prussian Blue reported in these letters is as a blue pigment for painters. The letter of September 28, 1709 reported that (Christoph Joseph) Werner (11), a Swiss painter in Berlin, had used the blue color for a long time and that he had sent it to other painters in quantity (8). Recently, Bartoll et al. (12) showed in an investigation of paintings from the collection of King Friedrich II of Prussia (the grandson of Friedrich I) that Prussian Blue can be found in paintings from Watteau that were painted in Paris between 1710 and 1712. Prussian Blue was also detected in paintings produced in Berlin by Antoine Pesne and others, the earliest being from 1710 (12). However, the earliest painting in which Prussian Blue was identified by Bartoll and colleagues was the "Entombment of Christ" by the Dutch painter Pieter van der Werff (1666-1720), which was painted in 1709 in the Netherlands . As shown below, during this time Dippel lived in the Netherlands and was also producing Prussian Blue.

In addition to the Frisch letters, other correspondence of Leibniz referred to Prussian Blue. In his correspondence with Johann Bernoulli (1667-1748) between December, 1710 and December, 1711 (13), Prussian Blue was discussed. Another example is a letter from Paris (dated August 17, 1714), in which the writer Hasperg told Leibniz (14) that Homberg (15) wanted Leibniz to describe the procedure for production of Prussian Blue. This letter mentioned that Leibniz had previously written to Homberg about Prussian Blue. Hasperg also stated in this letter that he and Homberg did not know the identity of the inventor. He further told Leibniz that a German in the Netherlands with the name "Dipelius" was also preparing the blue color and that he had a sample of this color, which was not as beautiful as the blue color from Berlin. Thus, it is clear that during his stay in the Netherlands, Dippel, the second inventor indicated by Stahl (5), was also producing Prussian Blue, but of an inferior quality.

Dippel in Berlin and the Netherlands

According to Stahl (5), the invention of Prussian Blue took place in the laboratory of Johann Konrad Dippel (1673-1734) in Berlin. Documents from the period showed Dippel's name, variously written as Dippelio, Dipelius, or Dippelius. He was a theologian, alchemist, and physician. Many of his mostly theological books were printed under the pseudonym Christianus Democritus. (Further information on Dippel's life can be found in Ref. 16-18) (19).

Around 1700, after some years of theological dispute, Dippel became interested in alchemy. First, he concentrated on attempts to transmute base metals into gold and later turned to finding a universal medicine. He thought that a substance which he called animal oil, produced by destructive distillation of animal blood, would be this universal medicine. Aynsley and Campbell wrote of Dippel`s animal oil (18):

> A glance at the list of principal constituents is enough to convince one of the heroic nature of the cure.

In the autumn of 1704, he moved to Berlin, invited by Count August David zu Sayn-Wittgenstein (1663-1735), who was one of the leading figures at the court of King Friedrich I. Here he rented a palatial house for his alchemy studies. Johann Georg Rosenbach, also a radical pietist, was living in this house and took part in Dippel's experiments.

In the early 18th century, Berlin was a good environment for alchemists who claimed to be able to convert common metals into gold. However, if they were not able to deliver gold, it could become dangerous. Of the alchemists who were active at this time in Berlin, Johann Friedrich Böttger (1682-1719) and Domenico Emanuele Caetano (?-1709) are the most famous. In 1701 Böttger fled from Berlin to Saxony, where he was later involved in the invention of European porcelain. Caetano arrived in Berlin in 1705. Dippel participated in the first tests of the abilities of Caetano as an alchemist. In 1709 Caetano was hanged in Küstrin (20). Other alchemists active in Berlin at that time, mentioned by Frisch in his letters to Leibniz (8), included Felmi (or Felmy or Filmey) and Meder.

Nothing specific is known about the alchemistic work of Dippel in Berlin. In early 1707 Dippel was arrested and held for about a week in the Hausvogtey prison at the request of the Swedish ambassador. Dippel had published a new theological book, which contained some harsh criticism of the Swedish Lutheran church. He was released on bail provided by Count Wittgenstein and soon fled from Berlin to the Netherlands. Living in Maarsen between Utrecht and Amsterdam, he worked as a physician for the next few years. From the letter of Hasperg to Leibniz, written in 1714 (14), it can be concluded that Dippel was also producing Prussian Blue during his stay in the Netherlands. He left the Netherlands in 1714 (21).

Since Dippel arrived in Berlin in the autumn of 1704 and left Berlin early in the year 1707, the invention of Prussian Blue most probably took place in 1705 or 1706. In a handwritten Berlin chronicle from approximately 1730 (22), the invention of Prussian Blue by the Swiss "Joh. Jacob Diesbach" is recorded for the year 1706. This date is the most probable year that is based on original sources.

The Secret is Out

Despite the efforts to conceal the production method of Prussian Blue, it remained secret for only about 20 years. In 1724 John Woodward published a procedure for the production of this color in the *Philosophical Transactions of the Royal Society* in London (23), and it was immediately followed by an account of some detailed experimental work on Prussian Blue by John Brown (24) in the same issue. The Woodward paper was based on a letter sent to him from Germany that disclosed the heretofore secret procedure, but Woodward did not publish the name of the author. Brown, a Fellow of the Royal Society since 1721, stated in his paper that (24):

> Dr. Woodward having lately communicated a paper (which he receiv'd from another hand) to this Society, containing a Process for making the Prussian Blue, I was willing to go thro' it exactly, according to the proportions there prescrib'd.

Obviously, John Woodward (1657-1728) (25), a physician, naturalist, and geologist, had asked the chemist Brown (?-1735) to perform some preliminary experiments to verify the contents of the paper he had received from Germany. In January / February, 1724 these two papers (23, 24) were communicated to the Royal Society and printed in the *Transactions*.

In his experiments Brown (24) not only followed the method communicated by Woodward, but also varied the procedure by precipitation of alternative metal hexacyanoferrate compounds, using silver, mercury, copper, bismuth (denoted as "Tin-Glass"), and lead instead of the iron used for preparing Prussian Blue. Thus, he performed the first documented research on the so-called Prussian Blue analogs, which continue to represent a major research field today. However, these experiments did not result in the beautiful blue precipitate that iron hexacyanoferrate gave. He also showed that in the calcination step, animal blood could be replaced by flesh ("beef") during the production process of Prussian Blue.

From whom Woodward received the information for making Prussian Blue is not clear and remains open to further investigation. Shortly after the two publications of Woodward and Brown, other people repeated the experiments and came to additional new conclusions. Notably Etienne-Francois Geoffroy (1672-1731) (26) in 1725 communicated to the French chemists the secret of the Prussian Blue production and published some new information (27-29). He found that Prussian Blue production could be achieved from other parts of animals such as horn, hair, skin, or hoof, in addition to dried blood and flesh (28).

With the secret of its preparation revealed, production of Prussian Blue began throughout Europe. Often it was sold under different names such as Paris Blue or Milori Blue, usually named after the production location, the owner of the facility, or based on an advertising idea (30). The production technology changed greatly over time. Asai analyzed about 100 methods published between 1724 and 1904 and documented the increasing improvements in product quality that resulted (30).

Prussian Blue was not only used as a pigment for painters but it was soon applied to the dyeing of textiles, following the work of P. J. Macquer (1718-1784) (31) conducted in 1749 toward this goal (32). Prussian Blue was also used for blueing textiles, is still used as a pigment today, and sold under the commercial name Iron Blue.

The Continuing Story of Prussian Blue

Starting in 1724 and continuing for about 250 years, chemists tried to define the composition, stoichiometry, and structure for Prussian Blue. Eminent scientists such as Priestley, Scheele, Berthollet, Gay-Lussac, and Berzelius were among the researchers in the field (33). In 1782 Scheele discovered hydrogen cyanide by heating Prussian Blue with diluted sulfuric acid (34), and in 1811 Gay-Lussac's determination of the composition of hydrogen cyanide (35) led to the conclusion that Prussian Blue contained cyanide. Because of the lack of modern analytical methods, the details of the crystal structure and even of the analytical composition of Prussian Blue were for a long time only partially resolved.

The first structural hypothesis for Prussian Blue was presented by Keggin and Miles with the help of X-ray powder patterns (36). Finally, in the 1970s Ludi et al. (37) published a detailed structure and confirmed the composition as $Fe_4[Fe(CN)_6]_3 \cdot xH_2O$ (x = 14-16), which is now accepted as correct.

The use of Prussian Blue as a painter's pigment in the early 18th century and as a dye for coloring textiles was followed by other uses. An important example is the cyanotype or blueprint process invented by Herschel in 1842 (38). This was a commercially successful photocopying process in use from 1843 until the early 1940s. Prussian Blue is also used in analytical applications, e.g., spot tests in the classical analytical chemistry of iron.

Prussian Blue has a very high affinity for thallium and cesium ions (39). Therefore, people who have become internally contaminated with radioactive thallium, nonradioactive thallium, or radioactive cesium can be treated by orally administered Prussian Blue, which traps thallium and/or cesium in the gut and thereby increases fecal excretion. Thus, the biological half-life of thallium and cesium is significantly reduced after capture therapy with Prussian Blue (39).

In 1978, Neff published a short notice in which he described the electrochemical deposition of thin films of Prussian Blue from aqueous precursor solutions onto conducting substrates. These films can be switched reversibly by electrochemical means between different colored oxidation states (40) in a process called electrochromism. Especially interesting for practical use is the alternation between colorless and blue oxidation states. One possible new application is the construction of so-called smart windows which can reversibly change their transmission of light between very high and low values (41).

Another technically interesting property of Prussian Blue is its ability to catalyze the reduction of hydrogen peroxide and molecular oxygen (42). Current investigation is underway to employ this effect for the construction of sensors for clinical, environmental, and food analysis (43). Prussian Blue also holds some potential as an active material in modern batteries (44) or as an electrocatalyst for fuel cells (45).

Conclusions

Prussian Blue was discovered by Diesbach and Dippel between 1704 and 1707, but most probably in 1706 in Berlin. Written evidence indicates that Prussian Blue was produced at least between 1708 and 1716 in Berlin by Diesbach and Frisch, and that it was mainly sold by Frisch. Dippel also produced Prussian Blue during his stay in the Netherlands until 1714. Diesbach and Frisch tried to protect the secret of Prussian Blue production because of its great commercial success. Once the secret was given away in 1724, production and research started in various European countries. The use of Prussian Blue as a blue pigment still continues today. Although Prussian Blue has been known in the scientific community for 285 years and has attracted much research ever since, new and promising areas of application are still being explored today.

REFERENCES AND NOTES

1. The Royal Prussian Society of Sciences was founded in 1700 in Berlin under the name Electoral Brandenburg Society of Sciences. Gottfried Wilhelm Leibniz (1646-1716), residing from 1676 in Hannover who initiated the founding of this society, was appointed president, a post he held until his death. One year after the founding of the Society Elector Friedrich III. of Brandenburg crowned himself in Königsberg (the modern Kaliningad in Russia) the first king in Prussia (Friedrich I.), starting the short history of the Kingdom of Prussia (1701-1918). Therefore, the name of the Society of Sciences changed to Royal Prussian Society of Sciences. In 1744 it was renamed the Royal Academy of Sciences.
2. (J. L. Frisch ?), "Notitia Caerulei Berolinensis Nuper Inventi," *Miscellanea Berolinensia ad incrementum Scientiarum*, **1710**, *1*, 377-378.
3. Anon., "Nachricht von dem vor kurzem erfundenen Berlinerblau," *Physicalische und Medicinische Abhandlungen der Koeniglichen Academie der Wissenschaften zu Berlin*, **1781**, *1*, 95-97.
4. Stahl, a physician and chemist, was professor of medicine at the university in Halle from 1694 to 1715. Then he moved to Berlin to become appointed physician to King Friedrich Wilhelm I, the son of King Friedrich I. Stahl died in Berlin.
5. G. E. Stahl, *Experimenta, Observationes, Animadversiones, CCC Numero Chymicae et Physicae,* Ambrosius Haude, Berlin, 1731, 280-283.
6. Many of Leibniz' letters and those sent to him are preserved (about 15,000 letters to and from about 1,100 correspondents) and part of these preserved letters were already been published in the 19th century. Others are still waiting to be published. Since 2007, the correspondence of Leibniz is registered in the UNESCO world documentary heritage Memory of the World. In 1901, work was started on publishing a complete critical edition of Leibniz's writings and correspondence. Since then the Academy Edition ("Akademie-Ausgabe") has been publishing the different series of Leibniz's writings and correspondence, a task that will continue for an estimated 30 years to come. This Academy edition is being prepared today by four research centers (in Hannover, Münster, Potsdam, and Berlin) of two local German science academies (Göttingen Academy of Sciences and Berlin-Brandenburg Academy of Sciences).
7. Hannover was the residence of the Duke of Braunschweig-Lüneburg. Leibniz worked as Privy Counselor of Justice for the Duke.
8. L. H. Fischer, Ed., *Joh. Leonh. Frisch's Briefwechsel mit G. W. Leibniz,* Georg Olms Verlag, Hildesheim, New York, 1976 (reprint of the book from 1896).
9. The town of Wolfenbüttel was the residence of Anton Ulrich Duke of Braunschweig-Wolfenbüttel. Part of his time Leibniz worked for him as a librarian.
10. At this time, for preparing the very expensive natural pigment ultramarine ($Na_{8-10}Al_6Si_6O_{24}S_{2-4}$), the mineral lapis lazuli was imported to Europe from Asia by sea (ultramarine literally means 'beyond the sea') and further ground and processed in local factories. A process for the production of synthetic ultramarine was discovered in 1826.
11. His father was Joseph Werner (1636-1710), first director of the Academy of Arts in Berlin from 1696, who returned to Switzerland in 1706.
12. J. Bartoll, B. Jackisch, M. Most, E. Wenders de Calisse, and C. M. Vogtherr, "Early prussian blue: blue and green pigments in the paintings by Watteau, Lancret and Pater in the collection of Frederick II of Prussia," *Technè*, **2007**, *25*, 39-46.
13. C. I. Gerhardt, Ed., *Leibnizens mathematische Schriften*, Part 1, Ch. 3, "Briefwechsel zwischen Leibniz, Jacob Bernoulli, Johann Bernoulli und Nicolaus Bernoulli," Verlag H. W. Schmidt, Halle, 1855, 858-878.
14. G. W. Leibniz, *Sämtliche Schriften und Briefe*, Reihe I, Allgemeiner, politischer und historischer Briefwechsel, Transkriptionen November 1703-November 1716, n° 391, 471-472. (version from 14.8.2007)
15. Wilhelm (Guillaume) Homberg (1652-1715) was a German scientist born in Batavia (the modern Jakarta in Indonesia) and living in France from 1682.
16. J. C. Adelung, "Johann Conrad Dippel, ein indifferentistischer Schwärmer," in *Geschichte der menschlichen Narrheit*, Part 1, Weygand, Leipzig, 1785, 314-347.
17. K. Buchner, "Johann Konrad Dippel," in Friedrich von Raumer, Ed., *Historisches Taschenbuch*, 3. Folge, 9. Jahrgang, F.A. Brockhaus, Leipzig, 1858, 207-355.
18. E. E. Aynsley and W. A. Campbell, "Johann Konrad Dippel, 1673-1734," *Med. Hist.*, **1962**, *6*, 281-286.
19. Dippel was born at Frankenstein castle near Darmstadt in Hesse (Germany) in 1673. His family lived in a nearby village and fled during a French raid in the Franco-Dutch War (1672-1678) to the castle Frankenstein. He studied theology in Giessen (Hesse, Germany) from 1689 to 1693 and in Strasbourg (Alsace, France) from 1695-1696. In Strasbourg he became a radical pietist. Pietism was a movement within Lutheranism at that time. From Strasbourg he moved back to Hesse in 1696.
20. This is now Kostrzyn in Poland, a town with a big Prussian fortress and prison at that time.
21. He had to leave the Netherlands again, because of a theological book which contained religious opinions that were not tolerable even in the Netherlands. Dippel next moved to Altona, at that time a Danish town. Today it is part of Hamburg, Germany. From 1719 until 1726 he was imprisoned on the Danish island of Bornholm. In 1726 he moved to Sweden but was forced to leave in 1728. He spent the last years of his life near castle Berleburg by Casimir von Wittgenstein, not far from the border to his home country Hesse.
22. J. E. Berger, *Kernn aller Fridrichs-Städtischen Begebenheiten*, manuscript Berlin State Library - Prussian Cultural Heritage, Ms. Bor. Quart. 124, Berlin, ca 1730, 26.

23. J. Woodward, "Praeparatio Caerulei Prussiaci ex Germania missa ad Johannem Woodward," *Philos. Trans. R. Soc.,* **1724**, *33*, 15-17.
24. J. Brown, "Observations and experiments upon the foregoing preparation," *Philos. Trans. R. Soc.,* **1724**, *33*, 17-24.
25. John Woodward was appointed professor of medicine in Gresham College in London.
26. Etienne-Francois Geoffroy was a French physician and chemist best known for his affinity tables.
27. Anon., "Sur le Bleu de Prusse," *Hist. Acad. R. Sci.,* **1725**, *33-38*.
28. É.-F. Geoffroy, "Observations sur la Preparation de Bleu de Prusse ou Bleu de Berlin," *Mém. Acad. R. Sci.,* **1725**, 153–172.
29. E.-F. Geoffroy, "Nouvelle Observations sur la Preparation de Bleu de Prusse," *Mém. Acad. R. Sci.,* **1725**, 220–237.
30. C. Asai, "'Handmade' Berlinerblau," *ZKK Zeitschrift für Kunsttechnologie und Konservierung*, **2004**, *18*, 268-292.
31. Pierre Joseph Macquer, a French chemist, was the author of the first chemical dictionary (1766).
32. P. J. Macquer, "Mémoire sur une nouvelle espèce de teinture bleue, dans laquelle il n'entre ni pastel ni indigo," *Mém. Acad. R. Sci.,* **1749**, *255-264*.
33. L. J. M. Coleby, "A History of Prussian Blue," *Ann. Sci.*, **1939**, *4*, 206-211.
34. C. W. Scheele, "Über die färbende Materie in Berlinerblau," *Neue Schwed. Akadem. Abhandl.*, **1782**, *3*, 256-266.
35. J. L. Gay-Lussac, "Recherches sur l'acide prussique," *Ann. Chim.*, **1815**, *95*, 136-231.
36. J. F. Keggin and F. D. Miles, "Structures and Formulae of the Prussian Blues and Related Compounds," *Nature*, **1936**, *137*, 577-578.
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