ADDENDUM TO "ON THE DISCOVERY AND HISTORY OF PRUSSIAN BLUE"

Alexander Kraft, Gesimat GmbH, Berlin; kraftalex@aol.com

In my 2008 article "On the Discovery and History of Prussian Blue" (1) I reported the story of the invention of Prussian Blue by Johann Jacob Diesbach (about 1670-1748) (2) and Johann Konrad Dippel (1673-1734) in Berlin in 1706 as told by Georg Ernst Stahl (1659-1734) in his book *Experimenta, Observationes, Animadversiones, CCC Numero Chymicae et Physicae* from 1731 (3).

According to Stahl, Dippel produced his later "infamous" animal oil ("oleum Empyrevmaticum animale") in Berlin. For the rectification of the animal oil he mixed it with potash ("Sale Tartari"). After repeated distillation, the remaining potash was stored away in a glass container. This potash was contaminated with cyanide and/or hexacyanoferrate, which led to the precipitation of Prussian Blue when this source of potash was used by Diesbach for the production his red Florentine lake.

Meanwhile, an additional historical source has begun to speak: the diary of Johann Christian Senckenberg which is currently being transcribed and published online (4). Senckenberg (1707-1772) was a German physician, naturalist and collector based in Frankfurt am Main. As a young man he was a friend and admirer of Dippel, who was more than 30 years his senior. In 1732 Senckenberg visited Dippel twice in Berleburg, Dippel's last place of residence. In his diary, which includes entries from 1730 until 1772, Senckenberg also reported on his travels to Berleburg, including accounts of many stories which were told to him by Dippel. On August 22, 1732, Dippel reported to Senckenberg, among many other things, that once during his time in Berlin (1704-1707) he was preparing a large amount of a "sal volatile" by dry distillation of calcined sal tartari (potash) and dried ox blood. The remaining mixture of about six pounds of mixed sal alcali tartari and sal sanguine was not thrown away as Dippel would have done, but collected and stored away by Dippel's young assistant Rößer (5). However, on the label, Rößer had only written "Sal tartari" and not "ex Sale alcali tartari constans et sale sanguinis." A "Lieutenant dießbach" was working in Dippel's lab on the preparation of Florentine lake and other pigments. In need of sal tartari, he used the wrongly labeled previously heated mixture of calcined sal tartari and dried ox blood for the preparation of Florentine lake. A blue color "caeruleum Berolinense" (Prussian Blue) resulted. Without informing Dippel, Dießbach drew up a contract with some painters for the delivery of the new blue pigment. But he could not produce this material anymore after the source of contaminated sal tartari was finished. Therefore, he came to Dippel and reported his problem. Dippel told him to use sal tartari and bovine blood and it did work out.

So this is what Dippel himself reported to a friend about the invention of Prussian Blue. It differs somewhat from the story told by Stahl. Most important was the fact that the accidental formation of hexacyanoferrate was not a result of animal oil production but of the preparation of a sal volatile. Since Dippel was one of original inventors we should consider his story more to be credible than Stahl's.

Other newly discovered sources contain two recipes for Prussian Blue's preparation which circulated in Germany before the first printed publication (6) of a Prussian Blue recipe in 1724. The first of these recipes was found in Dresden in a collection of papers (7) which most probably were in the possession of Johann Friedrich Böttger (1682-1719). The second recipe was sent in 1722 in a letter from a Hamburg merchant, Detlef Klefeker (1675-1750), to Johann Friedrich Henckel (1678-1744) a physician, mineralogist and chemist in the mining town of Freiberg in Saxony, Germany (8). Both recipes are very similar.

According to Klefeker's recipe, dried ox blood was mixed with potash. The mixture was then calcinated and treated with water to produce a first solution. A second red-colored aqueous solution was prepared from alum and ground cochineal insects. A third aqueous solution was made from alum and iron sulfate. All three solutions were then combined. The resulting blue precipitate was washed with water and dried.

Obviously, it was not so easy to successfully repeat this experiment. In 1723 Henckel, an experienced chemist, reported in an article in a scientific journal published in Silesia that he was in the possession of a Prussian Blue recipe (perhaps the one sent to him by Klefeker) that used blood, potash, alum, vitriol of iron and water, but he was not able "to get the blue down from heaven" (9).

Both recipes were written up in German, and included the unnecessary preparation of a red cochineal dye (carminic acid) solution, which was mixed with the blood lye and the iron sulfate solution during the precipitation of Prussian Blue. Therefore, they differ from the first officially printed recipe from 1724 in which cochineal was no longer used (10).

References and Notes

- 1. A. Kraft, "On the Discovery and History of Prussian Blue," *Bull. Hist. Chem.*, **2008**, *33*, 61-67.
- 2. Information on Diesbach can be found in parish registers of three churches in Berlin: the New Church and the Jerusalem Church in the Friedrichstadt neighborhood and the Church at the Köpenick Gate in the Köllnische Vorstadt suburb. In all these records his name is always written as Johann Jacob von Diesbach. In 1708 his marriage with Eleonora Dorothea Müller, daughter of Conrad Müller is recorded. In this record Diesbach is described as former Lieutenant of the English army. In the same year two sons (the twins Johann Jacob and Conrad Gottlieb) were born. Diesbach's wife Eleonora Dorothea died in 1721. In 1732 a second marriage of a Johann Jacob von Diesbach is recorded. It is not clear if he is the inventor of Prussian Blue or his son. The wife was Maria Elisabeth Leuen, daughter of Johann Michael Leuen. In the same

year a daughter (Maria Dorothea Henriette) was born to the new married couple. The inventor of Prussian Blue died from a stroke in 1748 in Berlin at the age of 78 years. Therefore, it can be concluded that he was born about 1670.

- G. E. Stahl, *Experimenta, Observationes, Animadversiones, CCC Numero Chymicae et Physicae*, Ambrosius Haude, Berlin, 1731, pp 280-283.
- Universitätsbibliothek Johann Christian Senckenberg, Goethe Universität Frankfurt am Main, J. C. Senckenberg (1707-1772) – Diaries, Vol. 2, p 406, entry for Aug. 22, 1732, transcribed and edited by Vera Faßhauer http://senckenberg.ub.uni-frankfurt.de/p/5381590 (accessed July 22, 2016).
- According to Senckenberg's notes on Dippel's report, Rößer (whose first name is not known) later became a physician and resided in Hamburg.
- J. Woodward, "Praeparatio Caerulei Prussiaci ex Germania Missa ad Johannem Woodward," *Philos. Trans. R. Soc.*, **1724**, *33*, 15-17.
- "Berliner Blau zu machen," Verschiedene Rezepte und Konzepte, Staatliche Kunstsammlung Dresden (SKD) Archive PS, ca. 1708-1719, pp 42-44. This recipe is published in: A. Loesch, Ed., Sächsisch schwartz lacquirtes Porcelain, Sandstein-Verlag, Dresden, 2013, pp 179-180.
- D. Klefeker, "Aufrichtige Beschreibung der Berliner blauen Farbe, dem rechten Ultramarin ähnlich," *Mine*ralogische, Chemische und Alchymistische Briefe von reisenden und andern Gelehrten an den ehemaligen chursächsischen Bergrath J.F. Henkel, Teil 2, Dresden, 1794, pp 191-195.
- J. F. Henckel, "Von Herrn D. Joh. Fridr. Henckels, ..., aus Saltz-Kraut und Sode neu-erfundenen blauen Farbe," Sammlung von Natur- und Medicin- wie auch hierzu gehörigen Kunst- und Literatur-Geschichten, 1723 [for 1721], 18, 421-427.
- A. Kraft, "On Two Letters from Caspar Neumann to John Woodward Revealing the Secret Method for Preparation of Prussian Blue," *Bull. Hist. Chem.*, 2009, 34, 134-140.

About the Author

Alexander Kraft, Ph.D. in Physical Chemistry (semiconductor electrochemistry) from Humboldt University in Berlin, 1994, is co-founder and one of the managing directors of Gesimat GmbH, Berlin, Germany, a company that developed a smart switchable glazing incorporating a thin electrochromic Prussian Blue film. Before starting at Gesimat in 1998, he developed electrochemical water-treatment technologies and devices. He continued working in this field as a scientific adviser until 2006. His research on the history of Prussian Blue started in 2007.

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