Study of Prussian blue pigments by X-ray diffraction and X-ray absorption spectroscopy

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Prussian blue was accidentally discovered in Berlin in 1704. Because of its low cost the pigment enjoyed immediate popularity and was widely used by artists until 1970. However, the permanence of Prussian blue was already questioned by the mid-18th century, as the pigment shows a tendency to fade in the light [1, 2]. The degradation processes of Prussian blue in paintings are not completely understood, although the comprehension of these mechanisms can help for preventive conservation and restoration of paintings.

Prussian blue is a hydrated iron(III) hexacyanoferrate(II) complex that can contain ammonium, potassium or sodium ions. The intense blue color is due to an intervalence charge transfer between the two oxidation states of iron at 680 nm [3]. The physical properties of Prussian blue make its preparation difficult: because of its colloidal character the pigment frequently absorbs excess of starting material as impurities during the synthesis. The methods of preparation affect thus the permanence of the pigment in the way that they lead to the introduction of a certain amount of impurities [4]. Those impurities can be oxidized to supply electrons and photoreduction to a white compound called Berlin white may occur. Nevertheless, those redox processes in the Prussian blue compounds are still under debate and new synthesis mechanisms continue to be proposed [5]. Moreover, the redox reactions in Prussian blue films are completely reversible, while in paint layer a reversible fading is only observed in the short term.

We report here the synthesis of Prussian blue according to different preparation methods and the characterization of these pigments by X-ray diffraction and X-ray absorption spectroscopy at Fe K edge. A thorough comprehension of Prussian blue synthesis through centuries can help to better apprehend the degradation mechanisms of Prussian blue in paint layers.

References

- [1] B. H. Berrie, Prussian Blue in Artist's Pigments: A Handbook of Their History and Characteristics, 3, National Gallery of Art, Washington, pp. 191-217 (1997)
- [2] J. Kirby, The National Gallery Technical Bulletin 14, pp. 62-71 (1993)
- [3] M. B. Robin, Inorganic Chemistry 1 (2), pp. 337-342 (1962)
- [4] J. Kirby and D. Saunders, The National Gallery Technical Bulletin 25, pp. 73-99 (2004)
- [5] Bueno et al., J. Phys. Chem. C 112 (34) pp. 13264-13271 (2008)