

Characterization of non-aged and aged modern Prussian Blue pigments by Mössbauer Spectroscopy, X-ray powder diffraction and X-ray absorption spectroscopy

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Prussian Blue was accidentally discovered in Berlin in 1704. Because of its low cost Prussian Blue 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. 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 sometimes contains ammonium, potassium or sodium ions. The alkali-free Prussian Blue is commonly called "insoluble" Prussian Blue, while Prussian Blue with alkali cations is called "soluble". This appellation refers to the ease of the "soluble" Prussian Blue to be peptized as a blue colloidal sol, although any form of Prussian Blue is highly insoluble. The intense blue color is due to an electronic interaction between the two oxidation states of iron. This intervalence transfer band occurs when visible light is absorbed at 680 nm.

We report here the synthesis of Prussian Blue according to modern methods from the mid 19th and 20th centuries. 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 chemical composition was checked by EDX and PIXE. Several samples were characterized by Mössbauer spectroscopy, X-ray powder diffraction, and X-ray absorption spectroscopy. Commercial and synthesized Prussian Blues have similar chemical compositions but show significant differences in their crystalline properties, such as different local environments of the iron ions, crystallite sizes and granulometry. Those parameters depend on the preparation methods and their influence on the final pigment color was investigated.

Commercial and synthesized powder of Prussian Blue were mixed with gum arabic solution and painted out pure or mixed with lead white on canvas. The paint samples were placed in a weathering instrument SUNTEST CPS+ and exposed to a Xenon lamp (black standard temperature was around 35°C and the window glass filter for indoor ageing was used). In order to determine the eventual interaction with binder and canvas, Prussian Blue was also aged in powder form. After 1000 hours of light exposure no discoloration was noticed for the pure Prussian Blue samples neither in powder form nor painted on canvas. In contrast, Prussian Blue mixed with lead white shows a visible colour change.

Prussian Blue samples in powder were analyzed by Fe K-edge X-ray absorption spectroscopy at the DUBBLE beamline at the ESRF (Grenoble, France). We will present and discuss the preliminary results obtained on aged samples.