

Decoding the fading of Prussian blue pigment

An understanding of degradation and alteration processes in painting materials is essential for preservation and for art history issues. The task is complex however because of the highly heterogeneous character of a paint layer, which consists of a mixture of pigments and a binder on a support. All the components interact and influence the ageing process of the paint layer. The work described here is focused on understanding the discoloration over time of a particular pigment, Prussian blue, a synthetic pigment discovered in 1704 in Berlin.

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FURTHER READING

SYNTHESIS AND FADING OF EIGHTEENTH-CENTURY PRUSSIAN BLUE PIGMENTS: A COMBINED STUDY BY SPECTROSCOPIC AND DIFFRACTIVE TECHNIQUES USING LABORATORY AND SYNCHROTRON RADIATION SOURCE

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J. Synchrotron Rad. 20, 460 (2013)

RELATIONSHIP BETWEEN THE SYNTHESIS OF PRUSSIAN BLUE PIGMENTS, THEIR COLOR, PHYSICAL PROPERTIES, AND THEIR BEHAVIOR IN PAINT LAYERS

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J. Phys. Chem. C 117, 9693 (2013)

Because of both its very intense colour and its low cost, Prussian blue was widely used as a pigment in paintings until the 1970's. However, reports of discoloration already appear in eighteenth and nineteenth century books. The early preparation methods were rapidly recognized as a contributory factor in the colour changes of the pigment.

In collaboration with the Centre Européen d'Archéométrie de Liège, Belgium, we have conducted research to identify the reasons for these alterations in early paintings. Typical eighteenth century empirical recipes were reproduced at Liège (Ph. D. thesis L. Samain, University of Liège 2012). We studied the resulting pigments using a combination of spectroscopic and X-Ray diffraction techniques.

Prussian blue is known to be a hydrated iron(III) hexacyanoferrate(II) complex, with an ideal chemical formulae $\text{Fe}_4^{III}[\text{Fe}^{\text{II}}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$. It is now known that only two reagents are needed to produce Prussian blue by precipitation: an iron salt and an alkali hexacyanoferrate. However, the latter product was unknown in the eighteenth century and was indirectly obtained from the calcination of animal matter (dried ox blood) and an alkali. Even though the synthesis process is expected to be better controlled under modern laboratory conditions as compared to the situation in the eighteenth century, reproducing the old empirical recipes is problematic. Thus, the Prussian blue powders synthesized according to the early methods are variable in colour and composition. They are often poorly crystallized, even showing amorphous-like diffraction patterns, revealing the presence of nanostructured compounds (see Fig. 1(b)).

A set of complementary structural methods has been used to characterize these powders. Because traditional crystallography breaks down at the nanoscale, a Pair

Distribution Function analysis, a method used to study glasses, liquids and amorphous materials, was performed on high energy X-ray powder diffraction data, collected at the European Synchrotron Radiation Facility, Grenoble (beam line ID11). This analysis allowed the identification of two undesirable and until now undetected nanocrystalline reaction products in the synthesized pigments: an alumina hydrate and the ferrihydrite $\text{Fe}_{10}\text{O}_{14}(\text{OH})_2$. The ferrihydrite is orange in colour and, mixed with blue, explains the greenish tint taken by some samples.

Additionally in order to evaluate the light fastness of the synthesized pigments, the pure pigment powders were painted from arabic gum on watercolour paper and subjected to accelerated light exposure (Fig1(a)). The samples that exhibit the highest colour changes contain a large amount of the undesirable ferrihydrite impurity. They also are the least well crystallized, compare Figs 1(a) and (b) where the samples that discolour show strongly broadened X-Ray patterns. The paint layer turns green because upon prolonged exposure to light the Prussian blue phase tends to fade and the orange tint of the ferrihydrite then becomes more apparent.

In conclusion, the results presented herein help to better understand the numerous early reports of degradation of Prussian blue and directly relate the tendency of Prussian blue to turn green to the eighteenth-century preparative methods, which easily lead to the formation of a variable but substantial amount of an undesirable iron(III) oxide. This study also demonstrates the power of combined diffraction and spectroscopic techniques to answer the highly complex questions arising due to the intrinsically heterogeneous nature of real life materials.

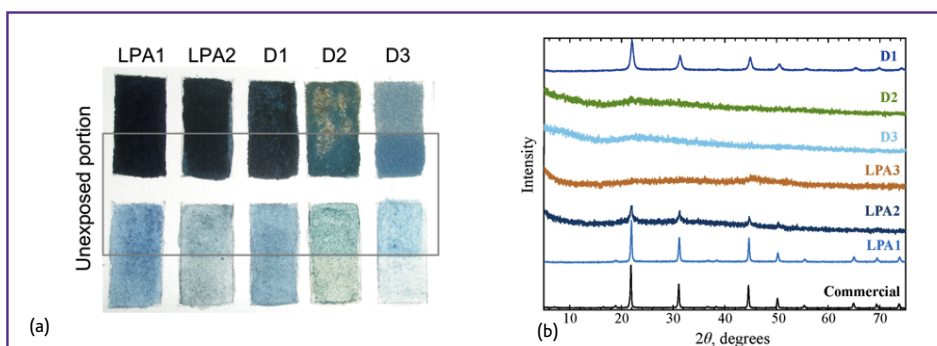


Fig. 1(a): Fading test on layers of the eighteenth-century Prussian blues, painted on watercolour paper : dark (top) and light shades (bottom). The rectangle delineates the location of the aluminium cover during the accelerated light exposure.

Fig. 1(b): X-ray powder diffraction pattern of some of the pigments shown in (a) with a modern commercial Prussian blue pigment given as reference (laboratory diffractometer, $\lambda_{\text{K}\alpha}$ Fe).