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Prussian blue: importance for the cultural legacy in Brazil, first identification, synthesis in the 18th century and degradation products

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Material cultural assets can suffer intentional damage and degradation inherent to the environment and time, compromising the history, memory and identity of societies. Thus, scientific studies of heritage are of great importance to assist historical studies, authorship, authenticity, preservation, conservation and restoration works. Prussian blue, iron(III) hexacyanidoferrate(II), was first synthesized in the early 18th century in Berlin, but its production was kept secret until 1724[1]. To date, no systematic study has been found on the circulation and production of Prussian blue in Brazil, which could be an important dating tool for artworks. Thus, physicochemical analyzes using energy dispersive X-ray fluorescence (EDXRF), scanning macro X-ray fluorescence (MA-XRF), Raman and infrared spectroscopy (FTIR) and scanning electron microscopy (SEM-EDS) were carried out in several artworks of Brazilian heritage in order to identify the use of Prussian blue. The Book of Commitment of the Irmandade de N. S. do Pilar do Mosteiro de S. Bento do Rio de Janeiro (1740) is the oldest document containing this pigment in Brazil. In a previous work[2], Prussian blue and its prussiates (degradation products that cause changes in the color of the pigment) had already been identified in a manuscript from 1750. In order to distinguish when these prussiates are formed, syntheses of Prussian blue were carried out based on the methodology described in the treatise The Handmaid to the Arts Teaching, v.1 (1758). The reproduction was carried out as closely as possible to the original description, using dried ox blood, alkali, alum and iron(II) sulfate as reagents. The alkali was obtained in this work from tree ashes lye and the compounds K_2CO_3, K_2SO_4, KCl, K_2O and SiO_2 in its constitution were characterized. In the synthesis of Prussian blue, a mixture of the pigment in soluble and insoluble forms was obtained, in addition to a possible mixture of prussiates. Amorphous carbon, KCl and alum were identified as subproducts. Seeking to understand a little more about the prussiates for the conservation of cultural assets, prototypes of watercolor paint on paper (19th century and current) were subjected to anoxia atmosphere testing, a non-toxic disinfestation method of great importance in conservation of museum collections. The Prussian blue pigment is an oxygen-sensitive compound, as its color depends on the intervalence charge transfer mechanism between the Fe(II) and Fe(III) ions present in its structure. After this test, reversible fading of the paints was observed based on colorimetric measurements of L*a*b*. However, by Raman spectroscopy it was possible to observe significant shifts to lower wavenumbers of the main Prussian blue band (~2155 cm^{-1}), associated with the ν(CN) stretching. This displacement is due to redox reactions involving the metal centers of the molecule and, consequently, to the formation of prussiates as degradation products. Therefore, in the long term and after several anoxia treatments, it is possible that the color change of Prussian blue-based paints becomes irreversible.

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References

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