DOI: 10.32703/2415-7422-2024-14-1-213-235

UDC 535.6:546:667: 75

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Prussian blue pigment: Bridging the historical palette to modern innovations

Abstract. *This comprehensive review explores the multifaceted realm of Prussian Blue, a pigment with a rich history and varied applications tracing its origins, artistic applications, and chemical properties. Beginning with its origins as a laboratory creation, the paper traces its evolution into a revered pigment in the artistic world. The review explores the electronic transitions responsible for Prussian Blue's deep blue hue, shedding light on the intricate chemistry behind its vivid coloration. Additionally, the pivotal role of iron ions in determining the pigment's properties is examined in detail, highlighting the importance of precise composition in achieving desired color characteristics. Challenges in the reintegration of Prussian Blue into conservation and restoration projects are also explored, emphasizing the importance of careful preservation techniques to maintain the pigment's integrity and vibrancy. The review discusses the pigment's lightfastness and stability, addressing common issues such as fading and discoloration over time. A notable phenomenon of bronzing particularly associated with Chinese Blue has been characterized by the appearance of yellow or brown hues on the surface of the pigment, that has puzzled artists and conservators for centuries. The review delves into the underlying causes of bronzing, examining factors such as environmental conditions, pigment composition, and application techniques. The review explores the pigment's interactions with other blues and whites, offering insights into the spectrum of shades achievable through careful color mixing and layering techniques. The paper revisits the perennial debate surrounding the permanence of Prussian Blue. While some argue for its enduring stability and* *longevity, others point to instances of fading and discoloration observed in historical artworks. The manuscript navigates these conflicting perspectives, providing an understanding of Prussian Blue's permanence in different contexts. Prussian Blue stands as a testament to the symbiotic relationship between science and art, where its molecular structure and vibrant shades continue to inspire both chemists in laboratories and artists in studios. The Prussian Blue emerges as a captivating convergence of art and chemistry that has left an indelible mark on laboratory benches and artists' canvases. The unique interplay of ferric and ferrous ions, not only renders a deep blue color but also makes it sensitive to the variation of its environment. The interplay of its refractive index, bronzing tendencies, and tinting strength shapes its artistic applications, influencing the vibrant hues it contributes to diverse palettes. The permanence paradox surrounding Prussian Blue underscores the importance of precision in its preparation. As artists mix and blend, the pigment unveils its versatility, playing a pivotal role in color harmonies and shade variations. Beyond its role in art, Prussian Blue finds diverse applications in medicinal and industrial contexts. From its use as an antidote for heavy metal poisoning to its incorporation into high-performance materials such as batteries and sensors, Prussian Blue continues to demonstrate its versatility and utility in modern society. The review highlights these varied applications, showcasing Prussian Blue's enduring relevance and evolution beyond its historical roots.*

Keywords: *Prussian blue synthesis; historical formulation; pigment stability; artistic application; impurities and additives; particle size and morphology*

Introduction.

Prussian blue, Fe $[Fe^{3+}Fe^{2+}(CN)_6]_3$, Iron (III)-hexacyanoferrate (II), has been heralded as an inaugural modern pigment since its inception in the early 1700s. The Prussian blue is a subject of both admiration and caution for colourists, as encapsulated by Linton in 1852: "a rich and fascinating pigment to the colourist, but not to be depended upon; and yet difficult to avoid" (Linton, 1852). Its historical significance is marked by various duplication such as potash or non-bronze blues, bronze blues (integral in printing inks), and dispersible blues, with its widespread production commencing around 1730. The incorporation of extenders like barium sulphate ($BaSO_4$) or calcium sulphate dihydrate ($CaSO_4 \cdot 2H_2O$) has given rise to a spectrum of pigments, occasionally referred to as Brunswick blues (Hasluck, 1916). Prussian blue's prevalence endured until approximately 1970 when it began yielding ground as an artist's pigment to phthalocyanine blue. This evolution, captured by the transition from Prussian blue to phthalocyanine blue, represents a pivotal shift in artistic pigments over time (Hasluck, 1916; Linton, 1852). In India, many historical works of arts from Himalayan regions to south west India including Rajasthan and Goa have been decorated using Prussian blue as artist palette that need proper conservation.

The inception of modern color can be traced back to the accidental discovery of Prussian blue in 1704 by the Berlin-based colour maker Diesbach. The pigment, resulting from Diesbach's experimentation with the oxidation of iron, marked a pivotal moment in the world of pigments. By 1724, Woodward documented the preparation of Prussian blue in England, solidifying its presence on the artistic palette (Woodward, 1724). The manufacturing process involved heating equal parts of saltpeter (KNO_3) and potassium tartrate in a red-hot crucible, followed by the addition of dry, powdered cattle blood. Incandescence ensued, and the resultant mass was washed with water. The wash water underwent treatment with a solution of alum ($K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$) and ferrous sulphate. The introduction of hydrochloric acid to the greenish precipitate yielded the distinctive Prussian blue color. Despite its high tinting strength, Prussian blue exhibits only moderate permanence to light and air. This iron-hexacyanoferrate pigment has remained a mainstay in the artistic realm since its availability to artists in 1724 (Kraft, 2009).

Prussian blue, discovered in 1704, has exhibited remarkable versatility in artistic applications. Its amalgamation with various pigments has yielded a spectrum of color and shades. Noteworthy mixtures include combinations with Naples yellow, yellow ochre, chrome yellow, and cadmium yellow, resulting in vibrant green paints. Additionally, the fusion of Prussian blue with bone black has been instrumental in achieving intensely deep black shades (Rogge & Bomford, 2022). Widely distributed since the early 1700s, Prussian blue held its status as one of the most commonly used blue pigments until approximately 1970. Phthalocyanine blue has since emerged as a prominent substitute in contemporary artistic endeavours, marking a shift in pigment preferences (Rogge & Bomford, 2022).

The use of Prussian Blue in Indian artworks is often associated with the British colonial period. During the British rule in India, which started in the late 18th century and continued for almost two centuries, there was an exchange of artistic techniques and materials between the East and West. Prussian Blue found its way into Indian art through this cultural interchange. The pigment's rich blue color and chemical stability made it appealing to artists working in various mediums. Indian artists started incorporating Prussian Blue into traditional paintings, miniatures, and other forms of art. It added a vibrant and lasting blue hue to their creations. The adoption of Prussian Blue also coincided with the decline of traditional Indian pigments like indigo, which was used for centuries. The new pigment became part of the evolving palette of Indian artists, contributing to the diversity of color in Indian artworks during this period. The use of Prussian Blue continued into the post-colonial era and the modern period. Today, it remains a significant part of the artist's palette in India, reflecting the continued fusion of traditional and modern elements in Indian arts. Fig. 1 shows use of Prussian blue in the mural art of 16^{th} to 17^{th} century Goa churches.

The aim of this comprehensive review is to explore the multifaceted state of Prussian Blue, tracing its origins, artistic applications, and chemical properties. By investing into its rich history and varied applications, the study seeks to shed light on the intricate chemistry behind its vivid coloration and the pivotal role of iron ions in determining its properties. Additionally, it aims to address challenges in conservation and restoration projects, while also examining the pigment's interactions with other colors and its diverse applications beyond the realm of art. Ultimately, the study aims to provide a holistic understanding of Prussian Blue's enduring relevance and evolution in both artistic and modern contexts.

Figure 1. Prussian blue used in the art works of Goa churches (Author's Figure).

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Color and Spectral Reflectance.

The distinctive color of Prussian Blue originates from an electronic transition, specifically from a low-spin Fe^{2}+ ion in a carbon-coordination centre to a high-spin Fe^{3}+ ion in a nitrogen-coordination centre. This transition occurs upon the absorption of visible light at 680 nm, generating an intense coloration with an extinction coefficient (ε) of 9800 mol^{-1} cm^{-1} (Goldanskii, 1967). This absorption phenomenon, known as the intervalence transfer band, is responsible for the striking coloration exhibited by Prussian blue. Despite its predominantly deep blue appearance, Prussian Blue can exhibit variations in undertones, leaning towards reddish or green hues. These variations are contingent on the preparation conditions, encompassing factors such as the oxidizing agent employed, reactant concentrations, pH levels, temperature, and batch size.

Iron blues, such as Prussian Blue, are susceptible to bronzing, a phenomenon where the color of the pigment appears to change or take on a bronze-like hue when exposed to certain environmental conditions, such as light, humidity, or pollution. This alteration can affect the appearance and stability of artworks or objects containing Prussian Blue pigment. This effect is attributed to the rapid rise in the refractive index of the blue pigment at the red end of the spectrum, becoming most apparent when observed at near-glancing angles (Creagh, Lee, Otieno-Alego, & Kubik, 2009). Bronzing is particularly noticeable in the pure pigment and is more pronounced in Chinese blues (Legnetti, 1984). This bronzed tone is valued in certain applications, such as in printers' ink. In a recent study, Haskovic & Ibragic, (2022) proposed Prussian blue as a pigment for retouching due to its ability to replace more fugitive pigments like indigo and, to some extent, blue copper pigments such as azurite. This recommendation is grounded in the pigment's stability and suitability for retouching applications.

Tinting strength and Infrared Absorbance.

The tinting strength of Prussian blue is notably high, particularly when compared to other pigments with low refractive indices (Briggs, 1918), mostly due to its superfine structure. According to Hurst (1902), a small amount, such as one-half ounce (42.5 gm), can perceptibly tint a substantial quantity of lead white, indicating its potent colouring ability. The refractive index of Prussian blue is reported to be 1.56 in blue light (McCrone, 1988; Taft, Mayer, & Kuniholm, 2000), and it possesses a cubic crystal structure. This relatively low refractive index makes it a transparent pigment suitable for glazing techniques in painting. Prussian blue exhibits extremely high absorbance in the photographic infrared region, ranging from 700 to 900 nm. The addition of less than 1% Prussian blue to a highly reflective white surface can reduce its reflectance by 50% (Scholz, Schröder, Gulaboski, & Doménech-Carbó, 2005). While generally lightfast, prolonged exposure to light can induce color changes in Prussian blue (Gettens & Stout, 1966). However, due to its intense color, Prussian blue can be challenging for reintegration, often requiring dilution or layering. The pigment's strong absorption of infrared radiation results in a dark appearance in infrared photographs. Fig. 2 shows the colour and structure of Prussian blue.

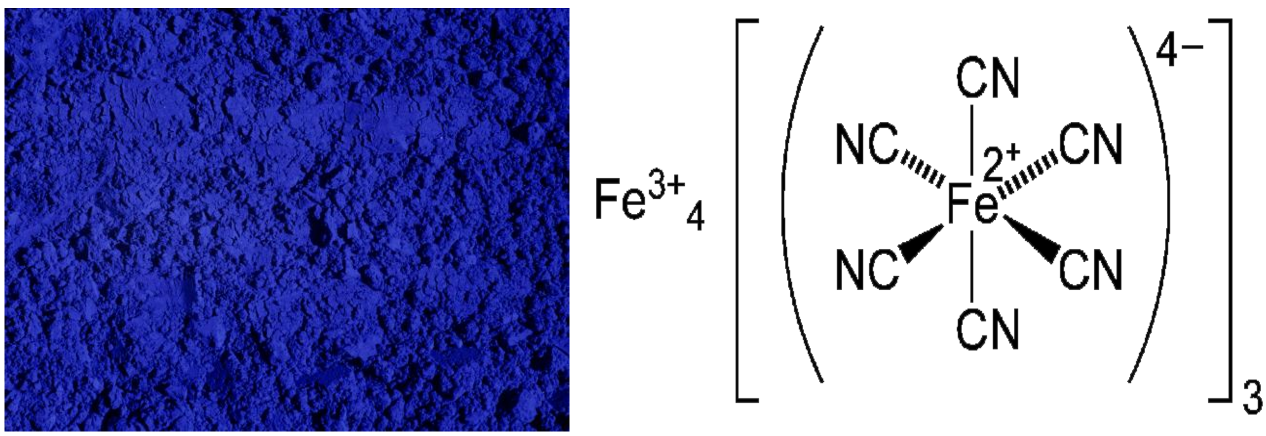

Figure 2. The Prussian blue colour and its atomic structure (Author’s Figure).

Ultramarine Blue, derived from lapis lazuli, has a deep blue color, high tinting strength, and good lightfastness with complex crystal structure (Roy, 2007). Cerulean Blue, known for its lighter and greenish shade has a lower tinting strength compared to Prussian blue. Cobalt Blue offers a bright, pure blue with moderate tinting strength. Ultramarine and Cobalt blues are known for their excellent lightfastness. Cerulean and Cobalt blues might be more forgiving in terms of reintegration due to their lighter tones. Indigo was historically significant in India as blue colorant and was used extensively for textiles (Fitzhugh & Winter, 1985). Lapis Lazuli was used for centuries, especially in Indian miniature and wall paintings.

The amalgamation of blue pigments with other blues or white is a prevalent artistic practice, yielding various shades and tones. The selection of pigments and their ratios significantly influences the resulting color. Ultramarine blue, renowned for its profound color, can, when mixed with titanium white, generate a spectrum of lighter blues, dependent on the proportion (Doerner, 1984). Titanium white has also been the base colour for Prussian blue. Cerulean blue, a lighter variant, combines with cobalt blue to produce diverse intermediate shades, embodying a balance of both pigments' properties (Gettens & Stout, 1966; Gottsegen, 2006). Cobalt blue, boasting a bright and pure tone, blends seamlessly with zinc white to create a softer effect, often employed for crafting pastel shades (Mayer, 1991).

The research and development of blue pigments by European countries have historically influenced various regions, including India. The European exploration and trade routes introduced pigments like Prussian blue and synthetic ultramarine to India. These pigments became part of the vibrant Indian art scene, influencing traditional artistic practices. The availability of new blue pigments expanded the color palette for Indian artists. Artists could experiment with a wider range of blues, contributing to the diversity and richness of Indian art. The introduction of synthetic pigments involved advanced chemical processes. Indian artists and craftsmen might have learned and adapted these techniques, contributing to the technological exchange. Understanding the properties and behaviours of new pigments also influenced art conservation practices in India. The adoption of European blue pigments might have influenced the visual language of Indian art and contributed to the synthesis of traditional Indian artistic elements with Western influences. The trade of pigments facilitated cultural exchange, contributing to a more interconnected global artistic community. Knowledge gained from European research on pigments, their stability, and degradation could have influenced conservation practices in India. Fig. 3 shows the Prussian blue modern application in India.

Permanence.

The assessment of Prussian blue's permanence has yielded conflicting perspectives. Kirby and Saunders (2004) and Heaton (1932) indicated a lack of permanence, advising caution, especially in mixtures. Prussian blue is not considered part of the permanent palette and is generally recommended to be avoided, particularly in mixed applications. Additionally, mixing Prussian blue with lead white may lead to discoloration and a greenish tone, although this might be a consequence of the medium yellowing rather than the pigment itself.

Figure 3. Prussian blue modern application in India (Author's Figure).

Iron blues, particularly Prussian blue, are susceptible to chemical reduction in the presence of reducing media. Reduction occurs when the pigment loses electrons, resulting in color loss. This decolourization can be corrected by exposing the paint to air, facilitating the re-oxidation of Prussian blue. The phenomenon of Prussian blue losing color upon exposure to light and regaining its blue hue when stored in the dark was first observed by Franz Fernback in 1834 and later by Field in 1845 (Kirby, 1993; Samain et al., 2011). Kirby's (1993) investigation into the fading and color changes of early Prussian blue provided valuable insights. However, caution was raised by Levison (1976), emphasizing that while Prussian blue is permanent in its pure form, it tends to lose permanence when mixed with white pigments. The permanence rating drops significantly when Prussian blue is mixed with titanium white, highlighting a potential vulnerability in certain compositions. The permanence rating drops from eight (permanent) when pure, to only four when mixed with 1:10 titanium white (Kemp Maer Jr., Beasley, Collins, & Milligan, 1968). However, the titanium white has also been the base colour for Prussian blue.

The permanence of Prussian blue has been influenced by variations in its preparation and the care taken by different manufacturers. Harley (1982) referenced an observation of yellow appearing when water was applied to Prussian blue watercolour cakes. This yellow color might have resulted from a water-soluble impurity, potentially yellow prussiate of potash, which is potassium Ferro cyanide. The function of Prussian blue as an anticaking agent could be attributed to its ability to absorb moisture from the environment. While it's true that Prussian blue can exhibit a yellowish hue when water is applied due to impurities like potassium ferrocyanide, this doesn't negate its moisture-absorbing properties. In fact, this absorption of moisture could help prevent clumping by keeping the surrounding environment dry. Earlier formulations of Prussian blue that have exhibited lower permanence compared to modern preparations due to a higher proportion of adsorbed impurities, possibly stemming from less efficient washing of the final product or the use of less pure starting materials. Even the modern preparation has the similar problems due to the colloidal nature of Prussian blue and its extremely fine particle size. Prussian blue can undergo oxidation to produce a dark brown ferric complex, Fe Fe $(CN)_6$, which is prone to auto-reduction. The formula Fe Fe $(CN)_6$ has also been associated with a compound known as Everitt's green. Chadwick and Sharpe (1966) proposed that Everitt's green, also known as Berlin green, is likely a result of the partial reduction of the fully oxidized brown material. The green color intensity implies the presence of at least low concentrations of Fe (II).

Chemical properties.

Since its invention, Prussian blue has been a subject of extensive study by chemists. Early work on its chemistry was summarized by Coleby (1939). Prussian blue can exist in two forms: as an insoluble polymeric ferric ferrocyanide or as an alkali ferric ferrocyanide. It is a stable and inert transition metal complex, belonging to the class termed type II mixed valence, and possesses semiconductor properties. The room temperature resistivity of Prussian blue is reported to be 10^7ohm cm (Robin, 1962). Additionally, the compound displays ferromagnetic behaviour at extremely low temperatures, below -267°C.

Prussian blue exhibits specific chemical properties. It dissolves in concentrated mineral acids, 10% oxalic acid, and decomposes in dilute alkali. The pigment is resistant to dilute (10%) mineral acids, polar and nonpolar solvents, fatty acids, drying oils, and plasticizers, demonstrating excellent bleed resistance. Prussian blue remains stable up to at least 140°C and may ignite at higher temperatures. According to the ASTM D93-52 (1990a) standard, the flash point of Prussian blue is reported to be in the range of 600°C to 615°C. Notably, the addition of hot sulphuric acid to Prussian blue results in the evolution of hydrogen cyanide. Prussian blue also exhibits zeolitic properties, acting as an ion-exchange resin that readily exchanges group I cations such as lithium, sodium, potassium, rubidium, and cesium (Estelrich-& Busquets, 2021).

Mossbauer spectroscopy (Fluck, Kerler, & Neuwirth, 1963) and photoelectron spectroscopy (Wertheim & Rosencwaig, 1971) provide insights into the coordination of low-spin iron(II) to six carbon atoms and high-spin iron(III) to the six nitrogen atoms of cyano groups in Prussian blue. The electrochemistry of Prussian blue has been comprehensively reviewed by Itaya, Uchida & Neff (1986) and additional information on the compound's chemistry can be found in the research work of Duncan & Wigley (1963).

Compatibility.

Prussian blue is very sensitive to alkali and cannot be used in fresco or alkaline media such as lime paints, sodium or potassium silicates, alkaline polymer emulsions, or casein paints. The use of any alkaline material such as a soap or ammonia in cleaning areas that were painted with Prussian blue is likely to be detrimental. When applied to

Prussian blue, these alkaline surfactants can lead to chemical reactions that alter the pigment's molecular structure. Specifically, the alkaline environment can induce hydrolysis of Prussian blue, breaking down its chemical bonds and resulting in color changes or degradation. Additionally, alkaline conditions can promote the leaching of metal ions from the pigment, further compromising its integrity.

Hasluck (1916) cautioned against using Prussian blue in distemper for the walls of new buildings containing lime or whiting, as the alkali could cause the blue to turn into a "dirty-brown colour" (Gervais et al., 2013). Studies on the effect of paper de-acidification on the color of Prussian blue have been conducted. Since Prussian blue was used to tone paper, testing should be done before using alkaline materials in treating blue paper or watercolours. The literature often mentions that Prussian blue can be mixed with all pigments except those that are alkaline, specifically calcium carbonate and lead white, although there is little evidence of any detrimental interaction in modern formulations. Kühn (1986) described the decolourization of Prussian blue in a mixture with zinc white. Prussian blue mixed with zinc yellow to give "zinc green" is converted to zinc ferrocyanide, destroying the paint's color (Samain et al., 2011). Parnell (1846) described Prussian blue's use as a dye for calico and indicated that Prussian blue lacked the essential fast dye requirement of "resisting the action of alkalis and soaps." The sensitivity of Prussian blue to alkali is exploited for micro chemical testing to identify the pigment. In modern formulations of Prussian blue, the addition of nickel improves its resistance to alkali (Hughes & Rowe, 1983).

Oil absorption and grinding properties.

The oil absorption of Prussian blue during grinding varies depending on the quality and type of Prussian blue used. Treatment with surfactants can cause drastic changes in the physical properties of Prussian blue, including oil absorption. Technical data supplied by Degussa (1974) showed a variation in oil absorption depending on the type of Prussian blue used, with a range of oil absorption for each formulation (Abel, 1999). The total variation for oil absorption of all types of Prussian blue was from 40 to 72 ml of oil per 100 g Prussian blue. The Kirk-Othmer Encyclopedia (Eckroth, Grayson, Kirk, & Othmer, 1978) listed 35 to 56 g oil absorbed per 100 g of Prussian blue. The National Institute for Standards and Technology (formerly the National Bureau of Standards) requirement for Prussian blue is a minimum of 48% by weight of Prussian blue in linseed oil. A large proportion of poppy seed oil, 65% to 110% (that is, 65 to 110 lbs. per 100 lbs. Prussian blue), is required (Schilling, 2005). The high proportion of oil required to produce a workable paint, combined with the low refractive index of Prussian blue, means that visible changes in the color of the medium are easily perceived, and changes in the color of the paint are often due to changes in the medium and not the pigment itself. These changes perceived in the colour of the paint is due to the increase in the refractive index which shifts the transparency / opacity of the medium.

It is challenging to mix Prussian blue in water-based paints, and artists often add alcohol to help form a good paint. Without alcohol, the particles of Prussian blue tend to "float" on the surface. Manufacturers use poly alcohols and surfactants to produce workable paints.

Prussian blue is a hard material and challenging to grind. During grinding, care must be taken to avoid overheating as it may possibly ignite. The formulation produced by the A. Milori Company, Paris, was the first to provide easily worked material. The differences in working properties and texture of different preparations usually depend on the handling of the immediately precipitated material since it tends to agglomerate rapidly. High moisture content makes it easier to produce smaller aggregates of the pigment. Some of the problems in grinding are thought to result from unremoved impurities that include excess starting material. Treatment with surfactants helps to remove impurities but markedly affects the physical properties of the pigment. Adding aluminium stearate to Prussian blue oil paint provides a smooth and workable texture (Eckroth, Grayson, Kirk, & Othmer, 1978).

Toxicity.

In 1710, Prussian blue was considered non-poisonous as it contained no arsenic, making it recommended not only for painting but also as a medicine (Estelrich & Busquets, 2021). Prussian blue is employed as a medicinal antidote to radioisotope and heavy-metal poisoning (Šimonović, Kargačin, & Kostial, 1986). Prussian blue is not listed in the 1982 Registry of Toxic Effects of Chemical Substances; no acute toxicity data exist. The pigment is listed in the GRAS File, the U.S. Food and Drug Administration's list of chemicals generally believed to be safe, CFR, 1991 (De Rovira Sr., 2017). Prussian blue is non-mutagenic in the Ames Salmonella test (Mortelmans & Zeiger, 2000). Due to its low toxicity, it is used in cosmetics. While Prussian blue does contain cyanide groups, its insolubility, tight binding of cyanide group with iron, stability, limited bioavailability, and low toxicity make it nontoxic in practical applications. However, it's essential to note that the dry pigment, being a colloidal powder, can be irritating to the lungs when inhaled, and caution should be exercised. Prussian blue burns and evolves cyanogen, which is highly toxic.

Composition.

Two formulas for Prussian blue are commonly given: $K\ Fe[Fe(CN)_6]$ and $Fe_4[Fe(CN)_6]_3$• Modern formulations of Prussian blue are $M'\ Fe_m\ Fe_n(CN)_6 \cdot nH_20$, where M' is a potassium (K^+), ammonium (NH^{4+}), or sodium (Na^+), and n = 14–16. Currently, the use of both sodium and ammonium ions predominates. The use of ammonium ions in the formulation was first introduced in the United States following World War I, when potassium was an expensive commodity (Sistino, 1973).

Due to the colloidal nature of Prussian blue, various surface-adsorbed ions are present, which can complicate analytical results. The correct formulation has been determined using x-ray diffraction methods (Buser, Schwarzenbach, Petter, & Ludi,

1977) and neutron scattering (Herren, Fischer, Ludi, & Hälg, 1980). These sources revealed the presence of interstitial water, water of crystallization, and adsorbed water molecules. Additionally, Wilde, Ghosh, & Marshall (1970) demonstrated that different preparations of Prussian blue contained impurities in the form of 5% to 15% Fe_2O_3.

The formulation of Prussian blue, where M1 is a potassium ion, has been referred to as soluble Prussian blue or soluble Turnbull's blue. Despite being described as soluble, this complex is insoluble; however, it is easily peptized, meaning it disperses readily in aqueous solutions. There was once a belief that using ferrous salts and potassium ferricyanide in manufacturing resulted in Turnbull's blue, while using ferric salts and potassium ferrocyanide produced Prussian blue. It is now understood that both methods yield the same compound identified as $Fe_4III[FeII(CN)6]_3 \cdot xH_2O$ (Chadwick & Sharpe, 1966). Adjusting the molar ratio of reactants to 1:1 yields $KFe[Fe(CN)_6]$. The ASTM (1990c) standard for the dry pigment, D261-25, reapproved 1987, allows for no extenders, organic color, or lakes. The maximum moisture content is 8%, and up to 5% of other materials may be added to improve the handling characteristics of the pigment.

Adulteration and Sophistication.

Prussian blue is available both as a pure pigment and in mixtures with extenders and bulking agents. The addition of extenders often results in the pigment being sold under a different name. These extenders include alum, iron oxide, calcium carbonate, calcium sulphate (gypsum), barium sulphate (also known as "heavy spar"), starch, alumina, magnesia (Riffault, 2023), and clay or pipe clay. Commercial mixtures of Prussian blue with zinc white were also sold, typically not under the name Prussian blue. Antwerp blue, as described by Riffault and colleagues, is a mixture of variable proportions of Prussian blue, alumina, magnesia, and zinc oxide. The earliest date of commercial mixtures with zinc oxide is unknown, but Feeser et al. (2012) mentioned the use of zinc white mixed with Prussian blue. Stillman (1905) provided a recipe for Prussian blue paint containing "1 qtr Prussian blue, 14 lbs terra alba or barytes to 1/2 gallon of refined linseed oil, or alternatively 1 cw Prussian blue, 1 qtr barytes, and 1 qtr whiting in linseed oil to consistency."

The addition of nickel or cobalt in formulations has been shown to reduce the sensitivity of Prussian blue to alkali (Holtzman, 1945), but the exact mechanism behind this phenomenon is not fully understood. However, one proposed explanation is that nickel ions may interact with the cyanide groups present in Prussian blue, forming stable complexes that are less susceptible to alkali-induced degradation.

Bersch (1901) previously defined Antwerp blue as a pigment prepared by precipitating "a solution of two parts of zinc sulphate and one to two parts of green vitriol (according to whether a pale or deep blue is desired) by a dilute solution of yellow prussiate." This was described as a mixture of Prussian blue with zinc cyanogen compounds (Zhang, Chen, Fu, Yan, Tao, & Yang, 2022). Similarly, Hurst (1892) provided a similar recipe for Antwerp blue and suggested that Brunswick blues

(Prussian blue mixed with barium sulphate) had largely replaced Antwerp blue (Friend, 1910).

Nickel-containing preparations have been used in architectural applications since about 1938 (Brown, 1968). These preparations have the formula $Ni_2Fe_2[Fe(CN)_6]$ h. A modification that substitutes zinc for nickel has also found minor use in architectural applications. Prussian blue has historically been utilized in mixtures with yellow pigments to produce green hues. One such commercial mixture is chrome green (or cinnabar green), which combines Prussian blue with chrome yellow ($PbCrO_4$) along with varying amounts of white pigments or extenders. Small rods or spheres (1-2 μm) of chrome yellow are coated with Prussian blue to give a green color. Chrome yellow, commercially available in the early 1800s, was often mixed with Prussian blue shortly thereafter (Kühn & Curran, 1986). The term Brunswick green, initially associated with copper compounds, was later applied to a mixture of chrome yellow and Prussian blue. Additionally, Prussian blue has been employed in the creation of zinc green pigments. The term Victoria green was used for a combination of zinc yellow and Prussian blue (Brown, 1968), although it was also applied to a mixture of zinc chrome green and hydrated chrome oxide (Kühn & Curran, 1986). Prussian blue has also been combined with organic yellows, white pigments, and extenders. For instance, a mixture of Prussian blue and gamboge has been referred to as Prussian green, malachite green (Gleason & Walker, 1969), or Hooker's green, finding use in both oil and watercolour painting. However, these pigments are now being replaced by more stable mixtures. Olive lake, a blend of a yellow lake and Prussian blue, was documented as well (Brown, 1968).

Monthiers blue, named after its discoverer (Monthiers, 1846), is a modified form of the formula resulting from the reaction of ordinary Prussian blue with ammonia (Eastaugh, Walsh, Chaplin, & Siddall, 2008). It has been described as having a finer color and increased durability. Monthiers blue is obtained from the oxidation of the precipitate formed by the action of ammoniac ferrous chloride upon potassium ferrocyanide, with a chemical formula of $(Fe_2)2Fe(CN)_6$ $6NH_3 9H_2O$. Additionally, Prussian blue has been prepared on substrates like mica to create pearlescent greenish pigments (Armanini & Johnson, 1977; Pfaff, 2008).

Modifications of Prussian blue to produce brown compounds have been described. Linton (1852) outlined one such modification to produce a pigment called Prussian brown. This process involved adding yellow prussiate of potash ($K_4[Fe(CN)_6]$) to a solution of copper sulphate, resulting in a rich chocolate-brown pigment. However, this pigment had the disadvantage of being "totally destroyed by alkaline solutions, which are frequently used as abstergents in picture-cleaning." Another method to obtain Prussian brown involves calcining (heating) iron blue, and the discovery of this method has been credited to Mr. Telfer (Wilkins, 1998). Calcining to produce a black pigment was described by J. F. L. Mérimée (Taylor, 1957).

Identification and characterization.

Optical Microscopy observation.

Prussian blue, regardless of its formulation, is characterized by an extremely fine particle size, typically ranging from approximately 0.01 to 0.2 μm in diameter (Keggin & Miles, 1936). The shape and size of Prussian blue aggregates depend on the manufacturing process and can vary considerably. It's important to note that these aggregates consist of submicron particles, which smear or clump when dry, resembling indigo in appearance (Wild, 1929; Stewart-Remington & Francis, 1954).

Dispersed Prussian blue appears transparent and may resemble a blue streak or flat flakes in transmitted light; in reflected light, it appears blue (Ašpergĕr, 1952). Clumps or aggregates of particles are opaque. Prussian blue shares this property with indigo and phthalocyanine blue. Due to its cubic crystallographic system, the particles are isotropic and completely extinguished between crossed polarizers (Coccato, Moens, & Vandenabeele, 2017). When pure pigments are examined at 100 to l,000 X magnification, this property distinguishes Prussian blue from indigo and phthalocyanine blue, which both have low birefringence. In practice, the individual particles are too small to resolve and the admixture of other pigments, which are often birefringent, make it extremely difficult to use isotropic behaviour to characterize Prussian blue. While this property can distinguish Prussian blue from indigo and phthalocyanine blue at high magnification, the small size of individual particles and the presence of other pigments complicate its characterization using isotropic behaviour. Fig. 4a illustrates the appearance of blue paint under an optical microscope, showing very few blue flakes among lead white particles. Welsh (1988) noted differences in the agglomerate shape of Prussian blue prepared using original recipes (with cattle blood) and more recent recipes.

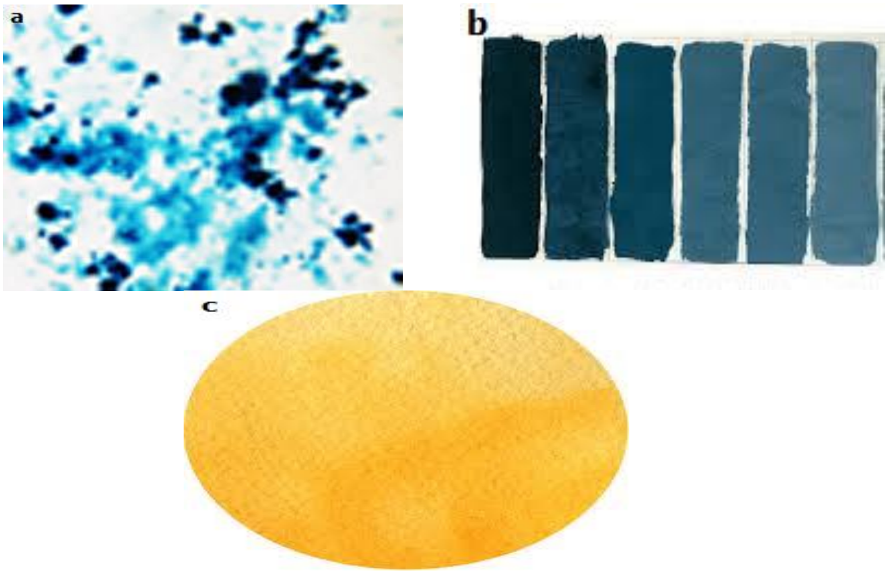

Figure 4. Optical image of Prussian blue *(a)*; Prussian blue colour on mixing different concentration of lead white *(b)*; Chrome green on mixing chrome yellow in Prussian blue *(c)* (Author's Figure).

The former consists of angular fragments of varying size, which could be mistaken for natural ultramarine. This highlights the challenge of identifying Prussian blue using optical microscopy. Large plate-like fragments of Prussian blue were found in many paintings by J. M. W. Turner (1775-1851) (Townsend, 1993). Schilling and Scott (1989) described the use of a Chelsea filter as an aid in distinguishing between ultramarine and Prussian blue, as reported by Mactaggart P. & Mactaggart A. (1998). A recent instrumental method to distinguish these pigments has been detailed by Gajić-Kvaščev et al. (2023). Fig. 4(a-c) shows the optical image of Prussian blue and colour of Prussian blue mixed with different concentration of lead white and chrome green colour on mixing chrome yellow in Prussian blue.

In the identification of Prussian blue, particularly within pigment mixtures, challenges arise due to its well-dispersed nature. For instance, a 5% by volume mixture of Prussian blue well dispersed in lead white, yielding a sky-blue tint when combined with linseed oil, may not be readily observable at normal magnifications using transmitted light microscopy (Peric, 2008). The presence of impurities, bulking agents, and extenders can contribute to birefringence, complicating the identification process.

Chemical identification.

Prussian blue can be effectively distinguished from other blue pigments through specific chemical tests. One distinctive characteristic is its sensitivity to alkali and its inertness to acids (Kraft, 2021). Upon the addition of 4M NaOH to Prussian blue, a rapid conversion to a brown compound occurs. In favourable instances, the blue color can be restored by introducing acid to the test mixture (Plesters, 1956). The presence of iron (III) in the alkaline solution can be confirmed by the formation of a red color upon the addition of ammonium thiocyanate. These tests enable the differentiation of Prussian blue from other blue pigments like ultramarine (both artificial and synthetic), phthalocyanine blue, and indigo. Notably, indigo is affected by dilute alkali only after prolonged heating or exposure, while the other mentioned pigments remain unaffected (Day, Herren, Ludi, Güdel, Hulliger, & Givord, 1980). Prussian blue can be distinguished from indigo and phthalocyanine blue through various tests. One common method is the Prussian blue test, where a sample is treated with hydrochloric acid, resulting in the formation of ferric chloride and a white precipitate. Another method involves the addition of potassium ferricyanide, which produces a characteristic deep blue color in the presence of Prussian blue. Additionally, spectroscopic techniques like X-ray diffraction can be used to identify the crystalline structure unique to Prussian blue. Upon ignition, it decomposes rapidly, leaving a residue of ferric oxide. Prussian blue demonstrates very good lightfastness. It is considered non-toxic. The pigment exhibits fair permanence in both light and air.

Crystal structure.

Prussian blue exhibits cubic crystal structure with isotropic refractive index. Under Optical Microscopy (OM) Prussian blue exhibits small particles with a discernible greenish hue. These particles tend to clump together, forming amorphous aggregates. From a technical standpoint, the pigment is a finely divided ferric ferrocyanide, resembling a dye in its microstructure. The particles are characterized as soft, with an average size of approximately 0.5 µm. Notably, Prussian blue is soluble in 10% oxalic acid.

Prussian Blue Synthesis Methods: A Comparative Overview.
Artificial Precipitation Method.

The artificial variety of Prussian blue is synthesized by precipitating a solution of potassium ferrocyanide with a more saturated solution of iron(III)-chloride. The crucial factor is the combination of ferric ions (from the chloride) with ferrocyanide, resulting in the formation of the pigment. Williamson (1845) emphasized the necessity of having the two irons in different oxidation states (ferric vs ferrous) for the successful synthesis. Ludi (1981) contributed to the understanding of the underlying chemical processes in this precipitation method.

19th Century Method.

Copperas (hydrated sulphate of iron) is dissolved in water and boiled. Nitric acid is added until red fumes cease, and sufficient sulphuric acid is introduced to clarify the solution. This results in the formation of per sulphate of iron. A solution of ferrocyanide of potassium is then added until precipitation occurs. The precipitate is washed with acidulated water and dried. García-Jareño et al. (1988) documented this 19th-century recipe.

Laboratory Synthesis (Fisher Scientific).

Fisher Scientific is a contemporary source for laboratory-grade Prussian blue. A solution containing 2g $FeCl_3$ in 100 ml deionized water is gradually introduced into a stirred solution of 1g $K_4[Fe(CN)_6]$ in 200 ml deionized water. The resulting blue precipitate is filtered and subsequently dried at an elevated temperature, approximately 100°C.

While both methods ultimately result in the formation of Prussian blue through precipitation, laboratory synthesis allows for greater control over the reaction conditions and the properties of the resulting pigment.

Conclusions.

In conclusion, this comprehensive review offers a holistic exploration of Prussian Blue, spanning its origins, chemical properties, artistic applications, and contemporary relevance. From its serendipitous discovery to its diverse applications in art, science, and industry, Prussian Blue continues to captivate and inspire. As we continue to uncover new facets of this enigmatic pigment, its legacy as a symbol of creativity, innovation, and discovery remains as vibrant as ever. Beyond artistic allure, Prussian Blue's ventures into medicinal antidotes and industrial applications. The paper illuminates the chemical intricacies and also the perceptible changes in color, the challenges of reintegration, and the dynamic interplay with other pigments. The knowledge gained can be scientifically applied in field conservation of artworks in the light of sensitivity of the pigments to certain chemicals.

Funding.
This research received no external funding.

Conflicts of interest.
The authors declare no conflict of interest.

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Прусський синій пігмент: Поєднання історичної палітри із сучасними інноваціями

Анотація. *Цей комплексний огляд досліджує багатогранний світ прусського синього, пігменту з багатою історією та різноманітними застосуваннями, простежуючи його походження, художнє використання та хімічні властивості. Починаючи з його походження як лабораторного винаходу, стаття відслідковує його еволюцію до пігменту, шанованого у світі мистецтва. Огляд досліджує електронні переходи, відповідальні за глибокий синій колір прусського синього, проливаючи світло на складну хімію його яскравого забарвлення. Крім того, детально розглядається важлива роль іонів заліза у визначенні властивостей пігменту, підкреслюючи важливість точної композиції для досягнення бажаних колірних характеристик. Також досліджуються проблеми повторного використання прусського синього у консерваційних і реставраційних проектах, наголошуючи на важливості ретельних методів збереження для підтримки цілісності та яскравості пігменту. У статті розглядається світлостійкість і стабільність пігменту, вирішуючи загальні проблеми, такі як вицвітання та зміна кольору з часом. Характеризується явище бронзування, особливо пов'язане з китайським синім, що проявляється у вигляді жовтих або коричневих відтінків на поверхні пігменту, яке здавна спантеличувало художників і реставраторів. Огляд занурюється у підстави бронзування, вивчаючи такі фактори, як умови навколишнього середовища, склад пігменту та техніки нанесення. Стаття досліджує взаємодію пігменту з іншими відтінками синього та білого, пропонуючи уявлення про спектр відтінків, досяжних завдяки ретельному змішуванню та технікам нашарування кольору. Робота знову піднімає давню дискусію щодо довговічності прусського синього. Хоча деякі дослідники стверджують про його стійкість і тривалість, інші вказують на випадки вицвітання та зміни кольору, які спостерігаються в історичних творах мистецтва. Рукопис розглядає ці суперечливі погляди, даючи розуміння сталості прусського синього у різних контекстах. Прусський синій стоїть як свідчення симбіотичних відносин між наукою і мистецтвом, де його молекулярна структура та яскраві відтінки продовжують надихати як хіміків у лабораторіях, так і художників у студіях. Прусський синій виникає як захоплюючий перетин мистецтва і хімії, залишаючи незабутній слід як в лабораторних дослідженнях, так і на художніх полотнах. Унікальна взаємодія іонів заліза не тільки надає глибокий синій колір, але й робить його чутливим до зміни навколишнього середовища. Взаємодія показника його заломлення, тенденцій до бронзування і фарбувальної здатності, формує його художні застосування, впливаючи на яскраві відтінки, які він додає до різних палітр. Парадокс довговічності прусського синього підкреслює важливість точності в* *його підготовці. Коли художники його змішують, пігмент виявляє свою універсальність, відіграючи ключову роль у колірній гармонії та варіаціях відтінків. Крім своєї ролі у мистецтві, прусський синій знаходить різноманітне застосування у медичних та промислових контекстах. Від його використання як антидоту для отруєння важкими металами до включення у високоефективні матеріали, такі як батареї та сенсори, прусський синій продовжує демонструвати свою універсальність та корисність у сучасному суспільстві. Огляд висвітлює ці різноманітні застосування, демонструючи тривалу актуальність і еволюцію прусського синього поза його історичним корінням.*

Ключові слова: *синтез прусського синього; історичне формулювання; стабільність пігменту; художнє застосування; домішки та добавки; розмір часток і морфологія*

Received 19.04.2024
Received in revised form 14.05.2024
Accepted 15.05.2024