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Cyanorhodotype

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Detection of Residual Hexacyanoferrate Species in Cyanotype Prints: Chemical Principles and Relationship to Copper-Based Image Formation

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Abstract

Cyanorhodotype originated in 2020 as an analytical procedure motivated by conservation concerns relating to the long-term stability of cyanotype prints. Its initial purpose was to detect chemically accessible hexacyanoferrate(III) residues retained within paper fibres after final washing. Compared with hexacyanoferrate(II), hexacyanoferrate(III) residues are more difficult to remove during aqueous processing and may require prolonged washing. Their persistence is of particular conservation interest because hexacyanoferrate(III) retains a degree of photosensitivity, and residual quantities could potentially contribute to undesirable photochemical changes over time.

The original procedure employed copper(II) ions (Cu^{2+}) as a detecting reagent, applied only after completion of washing. The resulting pink-to-red coloration revealed chemically accessible residues in nominally white areas of the print, without introducing additional hexacyanoferrate compounds. In 2021, following recognition of the reaction's chromatic potential, the addition of Cu^{2+} was transferred to the processing water for deliberate creative image formation.

Interpreting the colour response requires distinguishing the hexacyanoferrate(III) species introduced during cyanotype sensitization from the hexacyanoferrate(II) state associated with proposed copper-containing products. The relevant electron-transfer pathway and the identity of the precipitated phases remain unconfirmed by colour observation alone. Reaction conditions, possible potassium incorporation, and paper properties further affect the response. Comparison with FerroBlend clarifies the distinction between post-washing detection, originally motivated by conservation considerations, and deliberate chromatic image formation.

Physico-Chemical Basis of the Process

Cyanorhodytype is based on the introduction of copper(II) ions into a photographic support containing residual hexacyanoferrate species derived from the cyanotype process. In its original “analytical” application, the solution was applied to an already washed print.

Standard Cyanorhodytype Formulation

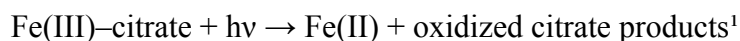
- Copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$): 0.5 g
- Sodium bisulfate (NaHSO_4): 1.0 g
- Water: to a final volume of 1.0 L

The formulation was designed to maintain a deliberately restricted ionic composition. Copper(II) sulfate supplies the metal ions required for the chromatic reaction, while sodium bisulfate establishes the acidic environment without introducing additional metal cations capable of participating in competing coordination or precipitation reactions. Potassium and hexacyanoferrate species are already supplied by the original cyanotype sensitizer. The choice of reagents therefore reflects a controlled chemical approach, intended to limit unnecessary variables within the photographic support.

Traditional cyanotype sensitization employs potassium hexacyanoferrate(III), $\text{K}_3[\text{Fe}(\text{CN})_6]$, together with an iron(III) complex, commonly ammonium iron(III) citrate. Hexacyanoferrate(III) species are therefore already present in the photographic support before cyanorhodytype treatment. The cyanorhodytype solution introduces copper(II) ions under acidic conditions but does not introduce additional hexacyanoferrate compounds.

Cyanotype is fundamentally a printing-out process (POP), in which the photochemical reactions responsible for image formation occur during exposure. The term *development*, when applied to cyanotype, is therefore used here in a broad operational sense, referring to the aqueous treatment through which soluble components are removed and the visible image reaches its final appearance.

The initial photochemical reaction involves the reduction of iron(III) complexes under ultraviolet irradiation:



The resulting iron(II) participates in reactions involving the hexacyanoferrate species already present in the sensitized paper, ultimately leading to the formation of Prussian Blue, the characteristic insoluble iron-hexacyanoferrate pigment responsible for the cyanotype image.

Hexacyanoferrate(III), commonly known as ferricyanide, has the formula $[\text{Fe}(\text{CN})_6]^{3-}$, whereas hexacyanoferrate(II), commonly known as ferrocyanide, has the formula $[\text{Fe}(\text{CN})_6]^{4-}$. Distinguishing these oxidation states is essential for interpreting the copper-induced coloration.

During aqueous processing, soluble sensitizer components are progressively removed from the paper. In practical cyanotype processing, hexacyanoferrate(III) residues can require more prolonged washing than the more readily removable hexacyanoferrate(II) species. Their elimination depends on diffusion through the cellulose fibre network, water exchange, and interactions with the substrate. The apparent whiteness of unexposed areas therefore does not necessarily indicate the complete absence of chemically accessible residual hexacyanoferrate species.²

The residual photosensitivity of hexacyanoferrate(III) makes its incomplete removal relevant to print conservation: retained material may contribute to undesirable changes during later exposure to light. Application of Cu^{2+} after the final wash provides a visible indication of accessible residues through the appearance of pink-to-red coloration.

The chemical response involves the interaction of Cu^{2+} with hexacyanoferrate species retained within the photographic support. The resulting reddish coloration has been associated with copper-containing hexacyanoferrate compounds, particularly those involving hexacyanoferrate(II).

Of particular interest is the mixed copper–potassium hexacyanoferrate(II) compound $\text{K}_2\text{Cu}[\text{Fe}(\text{CN})_6]$, whose crystal structure has been experimentally characterized.³ This compound demonstrates the possibility of potassium incorporation into copper-containing hexacyanoferrate coordination structures.

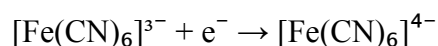
In the cyanorhodyotype system, however, the initial hexacyanoferrate species of analytical interest is hexacyanoferrate(III), originating from the original sensitizer. The formation of a compound containing hexacyanoferrate(II) would therefore require a change in the oxidation state of its iron centre.

The observed chromatic evolution of cyanorhodyotype suggests that the interaction between copper(II) ions and residual hexacyanoferrate(III) may proceed through successive chemical stages. The initially yellowish-green coloration, particularly evident at increased copper concentrations, progressively changes to salmon-pink during aqueous washing.

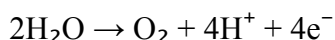
A particularly relevant analogy is provided by the chemistry of Prussian yellow, as described by Mike Ware in *Cyanomicon*. Ware explains that iron(III) hexacyanoferrate(III) forms a strongly oxidizing system which can undergo reduction through intermediate green states, ultimately yielding the more stable Prussian Blue. He further discusses how stabilization of the reduced coordination compound can substantially increase the effective oxidizing potential of the system, making the oxidation of water thermodynamically possible.⁴

The cyanorhodotype reaction exhibits a comparable sequence of chromatic changes, suggesting a chemically plausible analogy between the two systems. The initial interaction between copper(II) ions and hexacyanoferrate(III) may produce an unstable copper–ferri-cyanide intermediate whose subsequent reduction is favoured by the formation of a more stable copper-containing hexacyanoferrate(II) phase, possibly incorporating potassium. Although the redox properties of copper and iron hexacyanoferrates cannot be assumed to be identical, the mechanism described by Ware provides a relevant theoretical framework for interpreting the observed transformation.

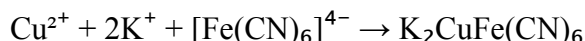
The required reduction is represented by:



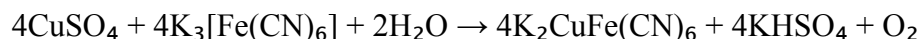
By analogy with the mechanism discussed by Ware, water may be considered a possible electron donor. Its corresponding oxidation would be:



The subsequent formation of potassium copper hexacyanoferrate(II) may be represented by:



Under this hypothesis, a formally balanced overall equation can be written:



This equation represents a proposed stoichiometric pathway rather than an experimentally demonstrated overall reaction. Its validity depends on whether the formation and stabilization of copper-containing hexacyanoferrate(II) can provide a sufficient thermodynamic driving force for water oxidation, as Ware describes for the corresponding iron system. Such a condition has not yet been established for cyanorhodotype.

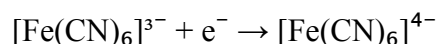
The hypothesis is supported qualitatively by the experimentally observed yellowish-green to salmon-pink transition and by studies documenting the redox behaviour of copper hexacyanoferrate compounds.⁵ The analogy with Prussian yellow offers a coherent framework for investigating these observations, but does not establish that the intermediate phases, electron-transfer pathways, or final precipitates are identical in the two systems. In particular, the participation of water as an electron donor remains a proposed mechanism requiring experimental confirmation.

In 2021, the copper-induced colour response was adapted for creative photographic image formation, as documented by works published in June of that year.⁶

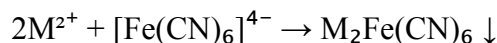
The chemical principle underlying cyanorhodytype may extend beyond copper to other transition-metal and post-transition-metal systems, potentially producing chromatic responses distinct from the characteristic blue of cyanotype. Many metal ions form poorly soluble, often coloured hexacyanoferrate compounds, whose properties depend on the metal involved, its oxidation state, and the resulting coordination structure.

A preliminary photographic application of this principle has been explored using lead(II) acetate, producing a deep greyish-blue image. This experimental variation has provisionally been named *Cyanoplumbotype*. Other potentially relevant systems include chromium and molybdenum, whose hexacyanoferrate chemistry suggests possibilities for different chromatic responses.

The generalization must begin with hexacyanoferrate(III), $[\text{Fe}(\text{CN})_6]^{3-}$, already present in the cyanotype sensitizer. Where the resulting metal-containing product incorporates hexacyanoferrate(II), its formation requires reduction of the original hexacyanoferrate unit through electron transfer:



For a divalent metal ion, M^{2+} , the subsequent formation of an insoluble metal hexacyanoferrate(II) can be represented by the idealized equation:



The two expressions describe successive conceptual stages rather than a universally established reaction mechanism. The electron required for reduction must arise from a corresponding oxidation process, whose nature may depend on the metal and the chemical environment. Moreover, the resulting coordination compounds need not conform to the idealized $\text{M}_2[\text{Fe}(\text{CN})_6]$ composition: mixed phases incorporating alkali-metal ions or metals in different oxidation states may also form.

This generalization therefore concerns the possibility of related electron-transfer and coordination processes, rather than the assumption that all metals undergo identical reactions or produce compounds of equivalent composition.

Residual Hexacyanoferrates and the Role of Washing

Washing removes soluble sensitizer components by mass transfer through the paper's porous structure. Its effectiveness depends on concentration gradients, water exchange, diffusion distances, and interactions between dissolved species and cellulose fibres. In practical cyanotype processing, hexacyanoferrate(III) residues are more difficult to eliminate than hexacyanoferrate(II) species and may require prolonged washing. Compounds located deeper within the fibre network may be removed more slowly than those near the paper surface. Consequently, a visually white region does not necessarily indicate the complete removal of chemically accessible hexacyanoferrate residues.

This behaviour is relevant to the long-term conservation of cyanotype prints. Hexacyanoferrate(III) retains a degree of photosensitivity, and its persistence within the paper raises the possibility of undesirable photochemical changes during subsequent exposure to light. The absence of visible staining after washing cannot therefore be regarded as conclusive evidence that potentially reactive residues have been eliminated.

The original cyanorhodyotype procedure, introduced in 2020, arose from these conservation concerns. Cu^{2+} was applied only after completion of the final wash, allowing chemically accessible residues remaining in the finished print to be detected through the formation of coloured copper-containing compounds. Applying copper during washing would address a different question, since soluble hexacyanoferrate species are normally present while unreacted sensitizer is being removed. The analytical objective was specifically to investigate their persistence after the washing process had been completed.

The post-washing response is qualitative unless independently calibrated. Colour intensity is influenced by the amount of accessible residue, copper concentration, treatment duration, precipitation kinetics, and the distribution, aggregation, hydration, and optical properties of the resulting solids. Increasing copper concentration may increase the extent of reaction when Cu^{2+} is limiting, but a linear relationship with colour density cannot be assumed. Precipitation may also alter local concentration gradients and the redistribution of soluble species. Thus, the visible pattern is not a direct measurement of the initial concentration of any single compound.

In 2021, the colour response was adapted for artistic purposes by adding Cu^{2+} to the processing water, allowing copper-induced coloration to become part of image formation. This treatment should be distinguished from the original post-washing analytical procedure in both purpose and interpretation.

Influence of the Paper Substrate

Paper is a chemically and physically active part of the system. Its heterogeneous cellulose network absorbs solutions and may retain dissolved constituents. Thickness, porosity, siz-

ing, and absorption capacity influence sensitizer distribution, washing efficiency, copper penetration, and precipitate localization. Commercial papers may also contain fillers and buffering agents; alkaline reserves, often based on calcium carbonate, can alter local pH and metal-ion behaviour.

Accordingly, two papers yielding visually similar cyanotypes may respond differently to Cu^{2+} under otherwise comparable treatment conditions. Substrate effects limit the use of colour intensity as a quantitative measure of residual hexacyanoferrate, but do not negate the qualitative diagnostic principle.

Relationship to FerroBlend

FerroBlend, introduced by Raghavendra Udupa, employs related copper–hexacyanoferrate chemistry to produce a deliberate combination of blue and reddish tones within a photographic print.

Standard FerroBlend Developer Formulation (Udupa)⁷

- Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$): 2 g
- Sodium citrate or potassium citrate: 10 g
- Water: initially 75 mL, then make up to a final volume of 100 mL

Compared with the standard Cyanorhodytype formulation (0.5 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 1.0 g NaHSO_4 per litre), FerroBlend employs a fortyfold higher nominal concentration of copper(II) sulfate pentahydrate. The two formulations also differ in their additional reagents: Cyanorhodytype uses sodium bisulfate to establish an acidic medium, whereas FerroBlend employs citrate as a copper-complexing agent. According to Udupa, the citrate is intended to limit unwanted staining and help preserve clean highlights.

The principal distinction, however, concerns the original purpose of the two procedures. Cyanorhodytype was introduced in 2020 as a post-washing analytical method for detecting residual hexacyanoferrate(III) species within the paper. Its subsequent creative application, developed in 2021, employed increased copper concentrations to obtain controlled chromatic effects while maintaining the tonal structure of the photographic image.

FerroBlend, by contrast, was conceived primarily as a colour-modifying process. Its copper treatment takes place during aqueous processing, when soluble constituents of the original cyanotype sensitizer may still be present.

The two procedures therefore share aspects of their underlying chemistry but differ in formulation, treatment sequence, and initial objectives. Their comparison provides a useful context for understanding the distinction between the analytical detection of residual substances and the deliberate use of related reactions for photographic colour formation.

Conclusion

Cyanorhodytype originated in 2020 from a conservation-related investigation into the persistence of hexacyanoferrate(III) residues within cyanotype prints after final washing. By introducing copper(II) ions as a detecting reagent, the procedure made it possible to reveal chemically accessible substances remaining in apparently white areas of the photographic support.

The subsequent creative adaptation of the process in 2021 extended the use of this chromatic reaction to image formation, with particular attention to tonal balance, highlight separation, and the preservation of clean whites.

The observed evolution from an initial yellowish-green coloration to salmon-pink suggests a sequence of chemical transformations rather than a single precipitation event. The analogy with the redox behaviour of Prussian yellow described by Ware provides a theoretical framework for interpreting this process, including the possible involvement of water oxidation. Nevertheless, the proposed mechanism and the composition of the resulting coordination phases require further experimental investigation.

The comparison with FerroBlend illustrates how related copper–hexacyanoferrate chemistry can be employed under different processing conditions and for different photographic purposes.

More generally, the behaviour observed in cyanorhodytype suggests that comparable interactions may occur between hexacyanoferrate species and other transition or post-transition metals. The extent to which such systems may reproduce analogous chromatic transformations depends on their individual coordination chemistry, redox behaviour, and precipitation conditions, providing a possible direction for further research.

Notes and references

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