On the So-Called ‘Hypo Cuprotype’

Physico-Chemical Limitations of the System Commonly Referred to as "Hypo Cuprotype": Ferric Ammonium Citrate / Copper(II) Sulfate/ Sodium Thiosulfate

The system under examination is based on the coupling between a ferric photosensitizer, ferric ammonium citrate (green type), and a mixture containing copper(II) and thiosulfate. The initial photochemical stage is well established: under *UV* irradiation, the ferric complex is reduced,

Fe(III)–citrate + hν → Fe(II) + oxidized products[1]

The resulting Fe(II) can act as a reducing agent toward copper(II), being oxidized back to Fe(III) while transferring an electron[2]:

$Fe^{2+} + Cu^{2+} \rightarrow Cu^{+} + Fe^{3+}$

Thus, **copper(I) is formed in the exposed regions**, while copper(II) remains predominant in the unexposed areas. The critical issue in this system is not the generation of the photochemical signal, but the fate of the copper(I) produced.

In the presence of thiosulfate, **copper(I) does not evolve toward an insoluble phase**, but instead enters into complexation equilibria. The predominant species are complexes such as:

$Cu^{+} + 2\ S_2O_3^{2-} \rightleftarrows [Cu(S_2O_3)_2]^{3-}$
$Cu^{+} + 3\ S_2O_3^{2-} \rightleftarrows [Cu(S_2O_3)_3]^{5-}$

The cumulative formation constants of these complexes are high ($\log \beta \approx 10$–13), implying that, at the operating concentrations of the system (thiosulfate on the order of 0.2 mol L^{-1})[3], the equilibrium is strongly shifted toward the complexed species.

This has a fundamental consequence: the system not only fails to produce a precipitate, but actively tends to maintain copper(I) in a dispersed state within the sensitized layer.

From a solubility standpoint, this behavior is consistent with well-established data for copper–thiosulfate systems. **Copper(I) thiosulfate complexes are water-soluble** and are exploited, for example, in hydrometallurgical processes for the dissolution of copper species. Under comparable conditions, copper concentrations on the order of 10^{-2}–10^{-1} mol L^{-1} can be sustained in a dispersed form within the aqueous microphases of the layer as a result of complexation[4]. This is incompatible with the formation of an insoluble image-forming phase.

The point can be stated directly: the reaction between Cu(I) and $S_2O_3^{2-}$ does not lead to the formation of a sparingly soluble salt, but rather to species whose thermodynamic stability increases the effective solubility of copper.

This behavior is the opposite of what is required in a functional photographic process. In a working system, the key reaction must result in a drastic decrease in solubility (precipitation or deposition). Here, the opposite occurs: complex formation increases the solubility of the photochemically generated product.

A comparison with **classical cuprotype processes** clearly highlights this difference. In that case, copper(I) generated during exposure acts as an intermediate which, during the wet treatment, reacts with thiocyanate:

$Cu^+ + SCN^- \rightarrow CuSCN(s) \downarrow$

Copper(I) thiocyanate is highly insoluble (Ksp ≈ 10^{-12}–10^{-13})[5], and its formation leads to a well-defined precipitation in the exposed areas. The solubility of the system decreases by several orders of magnitude, ensuring image stability.

In the **thiosulfate-based system**, by contrast, no transition toward a low-solubility phase occurs. Copper(I) remains in equilibrium with soluble or weakly retained species. As a consequence, in a semi-moist layer on paper, the material responsible for the image is not chemically fixed, but remains subject to redistribution and removal.

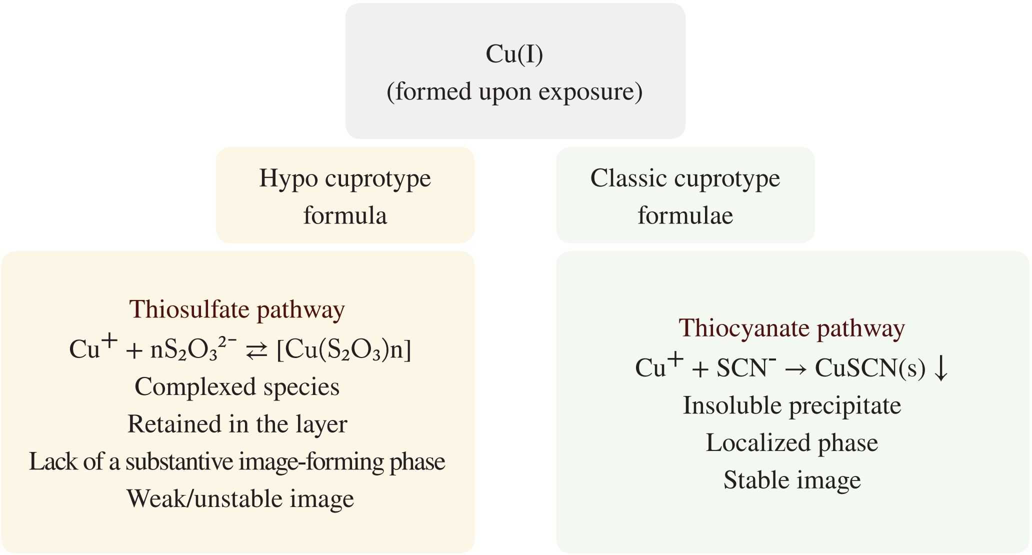
The observed behavior is consistent with this analysis. The native print is described as faint and low in contrast, indicating that the amount of material effectively localized in the exposed regions is minimal. Washing in water acts as an extraction step for soluble species:

$[Cu(S_2O_3)_2]^{3-}$ (aq) → removed

What remains on the support is largely determined by **physical retention** within the paper fibers. Image density therefore depends more on substrate parameters than on a chemically driven fixation mechanism. Empirical practices such as wetting the back of the sheet to increase density act by **enhancing absorption** and retention of the sensitizing solution, rather than modifying the underlying chemistry of the system.

The role of thiosulfate is thus intrinsically incompatible with direct image formation. Thiosulfate is a complexing ligand that stabilizes copper in a dispersed state and is used, in other photographic contexts, to increase the solubility of metal species. Its use as an image-forming agent therefore relies on an incorrect premise, namely that the copper–thiosulfate product is insoluble or sufficiently stable within the layer.

In conclusion, the limitation of the system is structural and arises from the fundamental chemistry of the Cu(I)/thiosulfate pair. The ferric photochemical sequence generates a real signal, but the subsequent complexation of copper(I) prevents the formation of an insoluble phase. In the absence of a decrease in the solubility of the photochemically generated product, neither selective image formation during the wet treatment nor chemical fixation can occur. The weak image observed is therefore consistent not with the formation of an insoluble compound, but with the partial retention of soluble species within the support.



Note

1. Mike Ware (2020), *Cyanomicon: The History, Science and Art of Cyanotype. Photographic Printing in Prussian Blue*, illustrated digital PDF edition, self-published, London, p. 327.
Available online: https://www.mikeware.co.uk/downloads/Cyanomicon.pdf

2. Ibid., p. 341.

3. F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann (1999), *Advanced Inorganic Chemistry*, 6th ed., Wiley, New York, pp. 851–853.

4. D. R. Lide (ed.) (2004), *CRC Handbook of Chemistry and Physics*, 85th ed., CRC Press, Boca Raton, Section 8, Stability Constants of Metal Complexes.

5. A. G. Sharpe (1992), *Inorganic Chemistry*, 3rd ed., Longman, London, pp. 469–472.