On the So-Called ‘Hypo Cuprotype’

Physico-Chemical Limitations of the So-Called "Hypo Cuprotype": Solubility, Complexation, and Substrate Effects

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Abstract

The system commonly referred to as "hypo cuprotype," based on ferric ammonium citrate, copper(II) sulfate, and sodium thiosulfate, is examined from a physico-chemical perspective. While the photochemical reduction of Fe(III) to Fe(II) and subsequent formation of Cu(I) are well established, the fate of the reduced copper species remains critical for image formation.

In the presence of thiosulfate, Cu(I) is strongly stabilized as soluble complexes, preventing the formation of a sparingly soluble phase. This behavior is incompatible with the requirements of a functional photographic process, in which image formation relies on a substantial decrease in solubility. The observed weak native image and its sensitivity to washing are consistent with partial retention of soluble or weakly bound species rather than with the formation of a distinct insoluble compound.

Alternative hypotheses, including the formation of copper sulfides through thiosulfate decomposition, are considered. However, these are not supported by the available evidence: the mild redox conditions do not favor significant sulfide generation, and the observed visual and chemical behavior is inconsistent with sulfide-based image formation.

The system further exhibits limited reproducibility and a strong dependence on the properties of the paper substrate. This suggests that image persistence is significantly influenced by substrate-driven retention mechanisms, potentially enhanced by factors such as porosity and the presence of an alkaline reserve.

Taken together, these observations indicate that the limitations of the system are structural and arise from the fundamental chemistry of copper–thiosulfate interactions, combined with the dominant role of the support in retaining image-forming material.

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.

$\text{Fe(III)–citrate} + h\nu \rightarrow \text{Fe(II)} + \text{oxidized products}$[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.

As a consequence, the system does not generate a precipitated phase, but instead maintains copper(I) in a dispersed form within the sensitized layer.

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 maintained in dispersed form within the aqueous microphases of the layer as a result of complexation[4]. This is incompatible with the formation of a stable image-forming phase.

In simple terms, the interaction between Cu(I) and $S_2O_3^{2-}$ does not produce a sparingly soluble compound, but rather species whose thermodynamic stability increases the effective solubility of copper.

This is contrary to what is required in a functional photographic process, where image formation relies on a marked decrease in solubility (precipitation or deposition). Here, complex formation instead enhances solubility.

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 ($K_{sp} \approx 10^{-12}$–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 bound 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 limited. 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 governed by physical retention within the paper fibers. Image density therefore depends more on substrate properties 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.

The role of thiosulfate is thus intrinsically incompatible with direct image formation. As a complexing ligand, it 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.

Assessment of Possible Sulfide Formation Pathways

An alternative interpretation that may be considered is the possible involvement of sulfur-derived species, leading to the formation of copper sulfides through partial decomposition of thiosulfate under irradiation or in the presence of metal ions.

The central question, in this context, is not the behavior of copper alone, but whether thiosulfate is reduced far enough to generate sulfide species in significant amounts. This represents a much stronger assumption than simple thiosulfate decomposition. Under the mild photochemical conditions of the process, such a conversion appears unlikely. The mere possibility of sulfur-containing decomposition products does not constitute evidence for effective sulfide generation, still less for sulfide as the dominant image-forming pathway.

In principle, thiosulfate can undergo decomposition processes yielding reduced sulfur species, including sulfide, which could react with copper(I):

$$2\ Cu^{+} + S^{2-} \rightarrow Cu_2S(s)$$

Such a pathway could, in theory, provide a route to the formation of an insoluble phase. However, several considerations limit the plausibility of this mechanism as the dominant process.

Under the actual conditions of the process—within a semi-moist sensitized layer on paper with a high local concentration of thiosulfate—the chemistry of thiosulfate is dominated by coordination to copper species rather than conversion into sulfide. The strong complexation equilibria involving Cu(I) and $S_2O_3^{2-}$ ($\log \beta \approx$ 10–13) are expected to suppress the availability of free sulfide species.

As already noted, if cuprous sulfide were formed to a significant extent, one should observe its characteristic visual signature: a dark (brown/black or at least dull) provisional image. This is not the case. The observed image is bright yellow, which is inconsistent with copper sulfides and instead suggests the presence of dispersed copper species or complexes within the layer.

Furthermore, copper sulfides such as Cu_2S are **highly insoluble** and relatively inert under mild conditions. If such a phase were responsible for the image, subsequent treatments—such as ferricyanide toning—would require prior oxidation or partial dissolution of the sulfide and would be expected to proceed slowly and incompletely. In practice, however, even faint residual images after washing can readily react with potassium ferricyanide, indicating that at least a fraction of the retained copper remains chemically accessible. This behavior is more consistent with weakly bound or dispersed copper species than with a compact insoluble sulfide deposit.

Finally, the persistence of an image after washing does not, in itself, constitute evidence for the formation of an insoluble compound. The paper substrate can retain soluble or weakly adsorbed species within its fibrous structure, leading to a residual image even in the absence of a true precipitation mechanism.

Taken together, these considerations indicate that, while sulfide formation cannot be entirely excluded as a secondary or localized process, it is unlikely to represent the dominant pathway responsible for image formation in this system.

Role of the Paper Substrate and Alkaline Reserve

The behavior of the system shows a marked dependence on the nature of the paper support, including porosity, sizing, and absorption capacity. Significant variations in image density, contrast, and overall appearance are observed across different papers under otherwise identical conditions. In particular, some substrates produce images with a characteristic chalky or matte appearance.

More importantly, the process exhibits limited reproducibility: even when nominally identical procedures are followed, the results are often inconsistent. This variability suggests that factors external to the nominal chemistry of the sensitizing system play a significant role in determining the final image. In systems based on the formation of a well-defined insoluble phase, a higher degree of reproducibility would generally be expected.

This sensitivity indicates that the retention of copper species is influenced not only by the chemistry of the sensitizing mixture, but also by the properties of the support.

A relevant factor is the presence of an alkaline reserve in many archival papers, typically based on calcium carbonate ($CaCO_3$). This introduces locally alkaline microenvironments within the fibrous structure, which can affect the behavior of dissolved or complexed metal species.

Under such conditions, copper may be partially immobilized through interactions with the substrate, including adsorption, ion exchange, or conversion into less soluble forms. These processes do not necessarily produce a well-defined precipitate, but can nevertheless result in a persistent and spatially localized image.

This interpretation is consistent with both the observed variability of the process and its strong dependence on paper type. It also provides an alternative explanation for image persistence after washing, without invoking the formation of a specific insoluble Cu(I) compound derived from thiosulfate chemistry.

In this framework, the paper acts as an active component of the system, contributing to the localization and retention of copper species. While this does not exclude additional chemical pathways, it indicates that substrate-driven effects play a significant role and should be considered in any mechanistic interpretation.

Conclusion

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 a well-defined insoluble phase. In the absence of a substantial decrease in solubility of the photochemically generated product, neither selective image formation during wet treatment nor true chemical fixation can occur.

The weak and often unstable image observed is therefore consistent not with the formation of an insoluble compound, but with the partial retention of soluble or weakly bound species within the paper matrix. This interpretation is further supported by the limited reproducibility of the process and its marked dependence on the properties of the support, which indicate that external factors—such as absorption, microstructure, and local chemistry of the substrate—play a significant role in determining the final image.

The system should therefore be understood not as a conventional precipitation-based photographic process, but as one in which image formation is largely governed by complexation and substrate-driven retention phenomena.

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.