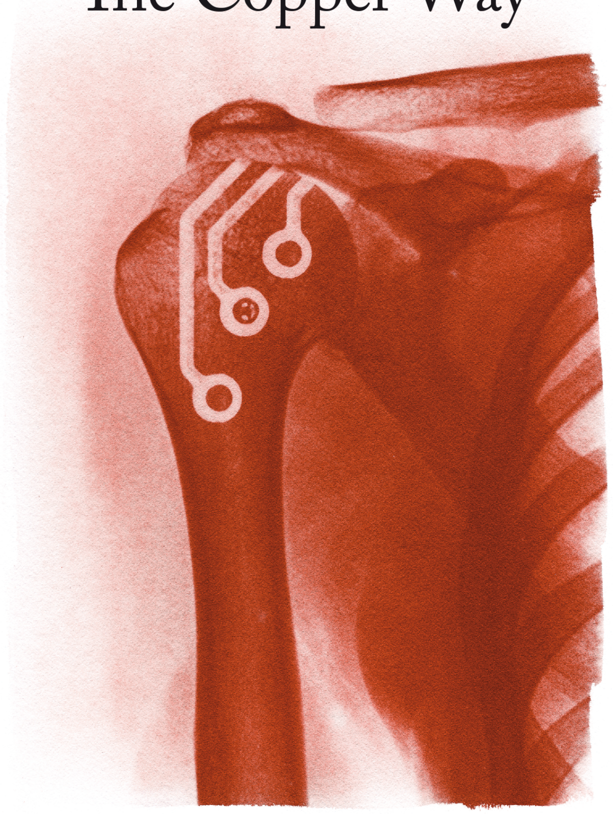
Vincenzo Caniparoli

The Copper Way



Cuprotype

Research on a Historic
Photographic Printing Process

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Vincenzo Caniparoli, "*Shoulder Tatoo*" *(Inner Conditions)*

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The Copper Way

Cuprotype

Research on a Historic Photographic Printing Process

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Introduction

I

I arrived at my first copper-salt print independently, in April 2020, by exploiting the different solubility of copper bromides.
Despite having been interested in historic photographic techniques for over a decade, until that time I had never heard of cuprotype. Only after an on-line search did I discover Patterson's method and, through it, the original historical processes of Burnett and Obernetter.

Of course, I am not the only one to have reached this goal by following a different path. As experience teaches, the methods for achieving a given result can vary widely, and many variants may exist of a single method.
In this book, everything related to the practice of cuprotype is filtered through my own experience; the information is therefore presented and discussed in light of it. It is thus necessary to emphasize that my ideas and methods may differ from the general opinions or practices of other experimenters devoted to this particular technique.

I decided to undertake the writing of this book after holding a workshop on cuprotype at the Academy of Fine Arts in Bari, organized by Professor Grazia Tagliente. This intention was fueled by the desire to set down in black—and "red—on white" the experiences gathered through experimentation devoted to this alternative historic photographic process.

Although scarce, there are already a few online articles about cuprotype, mostly referring to Patterson's method: the only truly noteworthy modern research dedicated to this technique. Aside from his excellent work—concise in detail but complete in its essence—others exist, though sporadic and not worth consideration here.

Only since 2020 has this process begun to appear in manuals of historic and alternative printing, and even then only briefly. As of February 2024, when I began writing this text, no book entirely devoted to cuprotype had ever been published.

This work therefore has a double genesis.
It was first conceived as a manual: a handful of historical notes accompanied by some technical and scientific information, and then a great deal of practice.

Modern literature on the subject, besides being scarce, proved to be inaccurate and full of gaps. In some cases, the historical sources themselves were ambiguous; one in particular helped to "contaminate" the original processes of both Obernetter and Burnett, a distortion that has been transmitted up to our own day.

Historical and modern documents also challenge the very chemistry of the reddish-brown pigment obtained in cuprotype, long believed to be Hatchett's brown. In seeking to reconstruct the origin of the inconsistencies among the sources, a new book emerged: a historical-scientific investigation rich in surprises, which in some cases revises long-held assumptions.

Archival research, extending beyond the strictly photographic context, has brought to light a considerable amount of information scattered across a constellation of documents, almost entirely in English and German. These fragments have made possible a coherent historical reconstruction of the process's origins and development, its limited diffusion, and its rapid oblivion, up to its modern rediscovery.

The practical sections of the text are based on my own experience, as is the experimental research. Where appropriate, my personal knowledge has been supplemented by the experiences of other experimenters.

Much more could have been added on technical and theoretical matters, but omissions were intentional. The goal was, from the start, to create a work that remains accessible in its technical and practical sections, without limiting it to those alone. It is an open-ended research project, in which the technical manual alternates with the historical and scientific reconstruction.

A cuprotype print—like any creative work in any technique—reflects the taste and skill of its maker. Yet it is not the mere use of an “exotic,” historic, or “alternative” photographic process that makes a print beautiful, nor does it make a photographer great. It is this mistaken habit of viewing mastery of the medium as the ultimate goal of the creative journey that leads many to criticize its overuse, rightly considering it a showy expressive gimmick.
Fortunately, in most cases, ambitions grow, and photographers themselves no longer settle for the mere technical expedient in order to progress.

This text may thus serve two kinds of readers: first, enthusiasts of historic photographic techniques, those photographers, both seasoned and novice, who find pleasure in experimentation and in the independent, manual production of their own works; and second, the naturally curious, beginning with students who, in their studies, choose or happen upon this “art.”

Vincenzo Caniparoli

Vincenzo Caniparoli

The Copper Way

Acknowledgement of Translation

The English-language text of this book was prepared by the author and benefited from the constructive assistance, careful review, and insightful suggestions of Dr. Lee Banting, Chris Hagen, Sophie Lascelles, and Dale Rio, whose contributions helped refine the English version.

Chris Hagen:
www.chrishagenstudio.com
www.greyhandpress.com

Dale Rio:
www.dalerio.com

To my family,
past and present.

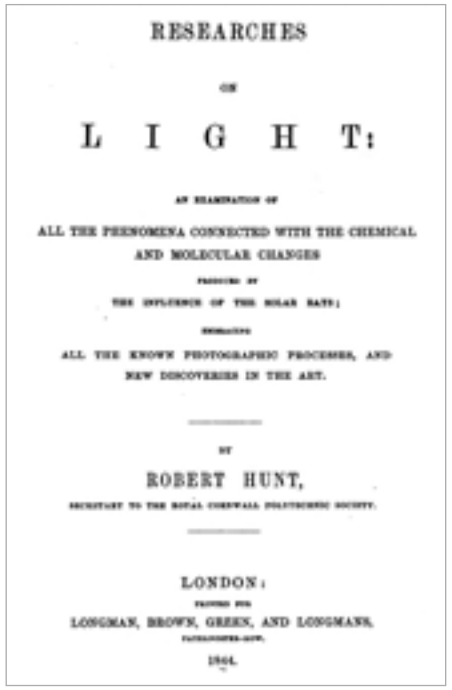
I

Red Signs:
Investigations from the Copper Age

Page 14: Photogenic Drawing (Artemisia)
Chromatype on Fabriano Rosaspina paper (285 g/m²).

Cuprotype: The Origins of the Process

The invention of photographic processes based on the light sensitivity of iron salts is certainly owed to **Sir John Herschel (1792–1871)**, whose research opened the path for many later discoveries. Equally undeniable, however, is the influence of another great scientist and photographic pioneer: **Robert Hunt (1807–1887)**.


RESEARCHES

LIGHT:

ALL THE PHENOMENA CONNECTED WITH THE CHEMICAL
AND MOLECULAR CHANGES

THE INFLUENCE OF THE SOLAR RAYS;

ALL THE KNOWN PHOTOGRAPHIC PROCESSES, AND
NEW DISCOVERIES IN THE ART.

ROBERT HUNT,

LONDON:

LONGMAN, BROWN, GREEN, AND LONGMANS,

1844.

Fig.1.1 — R. Hunt, Researches on light, first edition (1844).

To understand the context from which the **cuprotype** emerged one should begin from Hunt who studied in depth the effects of sunlight on a wide range of chemical compounds—particularly in relation to their photographic applications—published in **1844** his **Researches on Light**, where he presented a detailed investigations into the photochemical properties of numerous materials.

He focused especially on the photochemical behavior of **potassium bichromate,** with which he had already devised several photographic processes in combination with other chemicals—among them, the **chromatype**. This was a **direct positive process,** meaning it produced a positive image directly from the original, without the intermediate step of a negative.

The reproduction was achieved in a single exposure, a remarkably simple method,and the resulting images possessed such an appealing character that, although not sufficiently sensitive for use in the camera, they were considered of great value for copying botanical specimens, engravings, and similar subjects.[1]

In practice, the process involved immersing a sheet of paper in a solution of **copper sulfate**, then drying it; afterward, the sheet was immersed in a bath of **potassium bichromate** and, once dried again, exposed to sunlight. The image was developed in a **silver nitrate** solution and, as Hunt himself wrote, "*the result is a very pleasing positive picture*"[2]—a **red image on a yellow background**.

The process was presented at the **Meeting of the British Association for the Advancement of Science** in August 1843.[3] It relied on the light sensitivity of a copper salt—**copper chromate**—but under the action of a silver nitrate developing bath, the image was converted into **silver chromate**; therefore, not yet defined as a *cuprotype*.

Fig. 1.2 — Chromatype developed in a silver nitrate solution.

Fig. 1.3 — Chromatype bleached and redeveloped through direct darkening in sunlight.

From the Birth of the Term to the Development of the Technique

The term **cuprotype** ("copper print") was coined between 1856 and 1857 by **Charles John Burnett (1820–1907)**, an innovative photochemical experimenter and founding member of the **Photographic Society of Scotland (PSS)**.

The neologism initially referred to an evolution of **Robert Hunt's chromatype**, conceived almost fifteen years earlier. Burnett's new process was based on the same principles—using copper chromate as the light-sensitive compound—but unlike Hunt, he developed the print in **potassium ferrocyanide** solution. The resulting image was therefore composed of copper: **copper ferrocyanide**, a pigment known at that time as *Hatchett's brown*.

When considering the creation of the new term and the development of the associated process, it is useful to quote portions of a letter dated **July 10, 1857**, published by Burnett in *Photographic Notes* (P.N., vol. II, 1857):

> «I have experimented most extensively in many ways with the chromates and bi-chromates, and have succeeded, in various ways, in getting *very good* results. A very capital process, for many purposes, is to float or *steep* your paper in a mixed solution of bi-chromate of potash and sulphate of copper, as for Mr. Hunt's chromatype process, [...] but instead of developing it by a silver [nitrate] solution, as in the chromatype, wash out the salts unacted on by light, and develope by floating on a solution of ferrocyanide of potassium.»[4]

The print was then toned with iron salts in order to achieve a range that, at that time, were almost an exclusive feature of silver-based processes.
As Hunt had already experimented, Burnett suggested that using **copper chromate** directly as the photosensitive salt gave better results than the double bath of sulfate and bichromate:

> «I named bi-chromate of potash and sulphate of copper, in my letter to you as the most generally accessible forms of the materials for my Copper-Printing Process. I send you now a sample [...] of the separate chromate of copper. Dissolve this in ammonia, *sulphuric acid*, or, *best of all*, CHROMIC ACID, and you will find it, I think, more satisfactory than the bi-chromate of potash and sulphate of copper. [...] I send you also some sesqui-oxide of uranium [...] you will find it an excellent toning bath for the copper print.
> Use it either instead of the iron bath, when you will get prints of a richer brown than copper alone gives, and with purer lights than the forms of the uranium process described in my old paper, generally gives [...].»[5]

Of particular interest is the response by **Thomas Sutton**, the editor of the journal:

> «Your letter is really (in the chemical part of it), a mine of wealth. You have inundated us with good and useful suggestions.
> The process which you call the "Cuprotype," and of which you have kindly enclosed me a very nice specimen, is I think likely to prove an improvement on M. Sella's. Do pray make further experiments with it, and reduce it to something like a definite formula. It will then become your own "otype," and will not improbably be a most valuable one.»[6]


18 THE BRITISH JOURNAL ALMANAC ADVERTISEMENTS.

J. R. GOTZ'
List of Photographic Specialties.

THE OBERNETTER
GEL.-CHLORIDE OF SILVER EMULSION PAPER.
Three Tints:—White, Pink, and Mauve.
Acknowledged to be the finest Printing-out Paper ever produced, and giving PERMANENT PRINTS.
Can be treated exactly as Albumen Prints, the composition of the Toning Bath excepted.
To be had through any Photographic Stock Dealer, or Wholesale from the Consignee.

THE ROSE BRAND
DOUBLE BRILLIANT
ALBUMEN PAPER.
A Fine Quality DRESDEN PAPER. Wholesale only.
To be had through most Photographic Stock Dealers.

GOTZ'S FERRI-CYANIDE PAPER
FOR ENGINEERS AND DRAUGHTSMEN.
Direct Positive (Blue on White), by a simple process of Developing and Washing. Is superior to any similar production.

GOTZ'S FERRO-PRUSSIATE PAPER
BEST IN THE MARKET.
Fine, clear White Lines on Blue Ground, suitable for testing Negatives, &c. From most Photographic Stock Dealers.

J. R. GOTZ
19 BUCKINGHAM ST., STRAND, LONDON.
(See preceding page.)

Fig. 1.5 — Advertisement for Obernetter paper, British Journal Photographic Almanac (1888).

The German chemist's entrepreneurial venture was a **remarkable success**, marked by numerous celebrated inventions.

In **1868**, Obernetter became the first to **commercially produce collodio–chloride paper**, known as the *Aristotype*.[23] In 1869, he turned to collotype printing, giving it the form later known as *Albertotype*,[24] a technique he further refined through the **graphite dusting process**, which earned him a **gold medal** at the **Vienna Universal Exposition of 1873**.

By that year, Obernetter's company employed **twenty-two people**, operating **ten printing machines** and producing **high-quality collodion paper**.[25]

Between **1880** and **1882**, he formulated—and soon commercially manufactured—a **gelatin–silver chloride emulsion paper,** which achieved great reputation and widespread use.[26]

Together with **H. W. Vogel**, he developed what was likely his most important contribution: an **orthochromatic photographic plate** for landscape photography, capable of rendering **colored objects in correct tonal values.**[27] Alongside his technical production, Obernetter also worked as a photographic publisher.

Obernetter died suddenly of **cardiac syncope** at only **forty-seven years of age**, on **April 12, 1887.**[28] The sad news resonated internationally within the photographic community.

His research was continued by his son **Emil Obernetter,** himself a chemist and inventor, though the **ferro–cupric process** remained confined to the years of experimentation in **Josef Albert's laboratory**.

The Oblivion of the Twentieth Century

After Burnett and Obernetter, **interest in copper-based photographic processes** gradually faded. Occasional sparks of renewed attention toward cuprotype appeared,[29] but no one seems to have undertaken further systematic development of the technique.

The ferro–cupric process of Obernetter is also described in Duchochois's Photographic Reproduction Processes (1891).[30] However, Duchochois merely reproduced the formula and remarks of the German chemist—likely taken from *The Photographic News* article[31] of May 27, 1864—correctly dating the process to **1863**, the most probable year of its development.[32]

> It should be noted that in Duchochois's 1891 book there appears a **discrepancy in Obernetter's formula,** perhaps due to an earnest attempt at revision— or, more plausibly, a simple **transcription error**. The toning bath, originally composed of a **potassium ferrocyanide solution,** is rendered instead as **potassium ferricyanide.** This small but significant alteration would persist through later publications, with consequential effects that will be discussed further on.

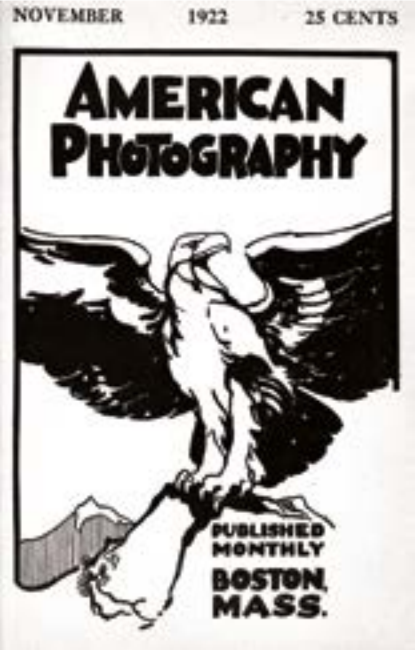


Fig. 1.6 — *American Photography*, cover, November 1922. Inside, Obernetter's process is mentioned in only four lines.

The late nineteenth century witnessed the emergence and rapid consolidation of new iron-based processes, most notably the platinotype, which, together with a wide variety of silver halide methods, effectively overshadowed these older "historic processes."[33]

By the **early twentieth century**, and with very few exceptions,[34] **cuprotype—**particularly Obernetter's ferro–cupric process—Burnett's copper chromate process having already vanished from collective memory—was relegated to the category of an **obsolete photographic curiosity**, a disused siding at the end of photography's railway.

At irregular intervals, it resurfaced briefly in photographic literature, only to fall back into obscurity after the **1920s.**[35]

Scattered reports exist of **occasional articles** in magazines and photographic manuals that this author has been unable to verify, either through accessible sources or private archives.
However, the **ferro–cupric process of Obernetter** does appear in the *Handbook of Alternative Photographic Processes* (1982).[37]

At the Turn of the Millennium

Although the practice of **alternative photographic printing processes** was never entirely abandoned, it remained confined to limited circles throughout most of the twentieth century.

After the mid-1990s, as the **Digital Era** definitively took hold—and within photography, the analog medium was being set aside (often with exaggerated relief)—a renewed interest in **historic photographic techniques** began to emerge.
Much of the credit goes to a small group of enthusiasts, photographers, and researchers who devoted their time and energy to reclaiming a forgotten body of knowledge, promoting its development and dissemination. Their work emphasized manual and artisanal craftsmanship in a world increasingly dominated by **automated industrial printing processes**.

A leading figure in this revival is undoubtedly **Dr. Michael J. Ware** (1939–), a chemist and photographer. Holding both a degree and doctorate from the **University of Oxford** and a member of the **Royal Society of Chemistry**, Dr. Ware began, after his retirement in 1992, a period of independent research dedicated to the **science, history, conservation, and art** of alternative photographic processes.

The results of his investigations—including major advances in **platinotype**, **cyanotype**, and **chrysotype**, as well as the invention of an entirely new process, the **argyrotype**—are recorded in more than seventy scholarly and popular publications in the photographic literature.[38]

In Italy, the **Rodolfo Namias Group**, founded in **Parma in 1991**, deserves special mention. Active nationwide, it organizes courses, exhibitions, and photographic events to **promote and disseminate knowledge of historic printing techniques**.[39]

A Refined Ferro–cupric Process

Dr. Ware's work on iron-based photographic processes (siderotypes) is of immense value. Perhaps never before had a scientist applied such rigorous passion to a niche field like historic photographic printing.
Free from commercial motivation, Ware undertook a meticulous redesign of several nineteenth-century processes. The platinotype, chrysotype, and cyanotype retained their historic names but were rebuilt from the ground up—replacing outdated reagents with modern, more efficient counterparts.
His descriptions of these modifications, supported by a wealth of quantitative data, form a comprehensive archive that has become foundational to the field's literature.

The same cannot be said for cuprotype, a topic Ware never addressed. The modern development of this process has no formal publication, apart from the recipe for the sensitizer, working solutions, and a brief procedural outline accompanied by a few historical notes.[40]

The ferro–cupric process of Obernetter was revived around 2007 by Dr. Jim Patterson, who held a scientific degree in pre-medicine with a specialization in chemistry.[41]
His formula and procedural notes first appeared in a mailing-list post dated October 15, 2007, published on-line at *altphotolist.org*.[42]

Written by **Christina Z. Anderson**, Assistant Professor at **Montana State University**, the message, titled Jim Patterson Cuprotype, contains information and related remarks about the process, written by Patterson himself.
Anderson reports that she met the creator the previous summer, during a workshop on the bromoil technique.

> «He was like a walking tome of chemistry information [...]. He kindly shares his formulas and notes on his development of the cuprotype [...][43]».

In essence, Patterson's contribution consisted of formulating a **new sensitizer**: replacing ferric chloride with **ferric ammonium citrate (green type)** as the light-sensitive compound, and substituting **copper(II) sulfate** for the chloride.

Compared with Obernetter's ferro–cupric process, several additional minor adjustments are introduced, which are described and analyzed in the next chapter.

For years his work remained part of **an underground network of online word-of-mouth** until the **COVID-19 pandemic**, when the long period of lockdown enabled broader dissemination. By 2020, images of prints made following his formula began appearing on-line.
In the same year, a fine article titled "**The Cuprotype Process**" appeared in *Guide to Photographic Alternative Processes*[44], in which Patterson's ferro-cupric process is described in detail, with a step-by-step guide through all its stages of preparation and development.

150 Years, Three Recipes

From **Burnett's process (1857)** to **Patterson's formula (2007)** spans exactly **one hundred and fifty years**.
These two procedures, together with **Obernetter's (1863–64)**, form the **three evolutionary stages of cuprotype**. While the similarity between Obernetter's and Patterson's processes is evident—essentially the same method, with the 2007 version as a modernized interpretation—the same cannot be said of Burnett's.

As previously discussed, Burnett's procedure, belonging to the inventor of the term cuprotype, **derived from Hunt's chromatype**.
But does that mean Hunt's process was itself a cuprotype?
Technically, no. The image substance in Hunt's process was **not copper-based** but consisted, depending on the developer used, of **insoluble chromates of heavy metals** such as silver, mercury, or lead, in hues ranging from red to orange and yellow.[45]

By definition, a **cuprotype** image must be composed of **copper** or a **copper salt**.
Literature identifies this compound as **cupric ferrocyanide**, a pigment known as **Hatchett's Brown**.

> Burnett, Obernetter, and Patterson each began with **different sensitizers** yet all ultimately achieved virtually the same result: a copper-based image.
> The same cannot be said for the **uranium–copper process** attributed to Burnett and described by **Duchochois**,[46] in which the resulting image consisted of a **mixed salt of copper and uranium**.

The Red–Brown Pigment

The pigment responsible for the **red–brown color** characteristic of the cuprotype is generally identified as **Hatchett's Brown**, named after its creator, the English chemist **Charles Hatchett (1765–1847)**. A cultured, affable man with wide-ranging interests, he was elected a member of the **Linnean Society (1795)** and of the **Royal Society (1797)**, two of Britain's most prestigious scientific institutions.

In **1801**, he discovered the chemical element now known as **niobium** (then called *Columbium*). Most of his scientific work was conducted between **1796 and 1806**[47].

Among his many publications, the one most relevant here is a brief **1802 article** describing his preparation of "**copper prussiate**", or **cupric ferrocyanide**, obtained by reacting **cupric chloride** with **calcium ferrocyanide** in aqueous solution. Hatchett described the product as an attractive brown pigment with a lilac tint.[48]

During the nineteenth century, **Hatchett's Brown** was widely used as an **inorganic pigment** in **oil and watercolor painting**, as well as in **wood coatings**.
Today, it appears under several different names, including:

- *Brown 9*
- *PBr9*
- *Florence Brown*
- *Florentine Brown*
- *Vandyke Red*
- *Hatchett's Brown*
- *Prussian Brown*

According to the Pigment Compendium (2004), all these designations refer to the same pigment originally developed by Hatchett and correspond to either **copper(II) hexacyanoferrate(II)**, $Cu_2[Fe(CN)_6]$, and **potassium copper(II) hexacyanoferrate(II)**, $CuK_2[Fe(CN)_6]$. The text further notes:

> «Copper may be substituted into the hexacyanoferrate(II) structure ('Prussian blue', q.v.) to give (according to the Colour Index, 1971) *dicopper hexacyanoferrate(II) hydrate*, (given as $Cu_2[Fe(CN)_6] \cdot xH_2O$), and/or a *dipotassium copper hexacyanoferrate(II)*, (given as $CuK_2[Fe(CN)_6]$). Terms associated historically with copper hexacyanoferrates include Hatchett's brown, copper brown and Vandyke red.»[49]

Already in *Field's chromatography* (Salter, 1869)[50] this pigment was considered chemically identical to **Prussian Blue**, except for the substitution of **copper** in place of **iron**.
In *The manufacture of mineral and lake pigments* (Bersch, 1901) **Hatchett's Brown** is described as **copper potassium ferrocyanide**. The author writes:

> «Hatchett brown is copper potassium ferrocyanide. It is obtained by precipitating a soluble copper salt with potassium ferrocyanide. Copper salts behave towards potassium ferrocyanide in the same manner as iron salts; different compounds result according as the ferrocyanide or the copper salt is in excess. Hatchett brown is somewhat largely used for painting wood.»[51]

Similarly, *A treatise on colour manufacture* (Mayer, 1908) explicitly associates **Hatchett's Brown** and **Vandyke Red** with **copper(II) hexacyanoferrate(II)**, $Cu_2[Fe(CN)_6]$. The preparation method mirrors Bersch's description—reacting **copper sulfate** with **potassium ferrocyanide**:

> «This compound is of a dark violet-red shade, with a brown tinge. It is still sometimes used as an artist's colour, but is very seldom found in trade as a material for paint.»

And again:

> «The shade can be imitated cheaply and very easily with red ferric oxide colours, and, indeed, Vandyke red has no specially advantageous qualities.»[52]

This final remark may explain why **Brown 9** is historically labeled as *Vandyke Red*, even though it is not the pigment generally regarded as the *true* Vandyke.
Here, the beginnings of the pigment's **terminological confusion** start to emerge.

Hatchett's Brown

In his **1802** article, Hatchett reported obtaining the pigment by reacting **cupric chloride** with **calcium ferrocyanide** in aqueous solution:

$$2CuCl_2 + Ca_2[Fe(CN)_6] \longrightarrow Cu_2[Fe(CN)_6]\downarrow + 2CaCl_2$$

Both Bersch (1901) and Mayer (1908) claimed that **Hatchett's pigment** could be produced by reacting a **soluble copper salt** (such as copper sulfate) with **potassium ferrocyanide** (then commonly called *yellow prussiate*).

However, it seems that **only Hatchett's original method** truly yields the **pure pigment**, consisting exclusively of **cupric ferrocyanide** (**$Cu_2[Fe(CN)_6]$**).
If this is correct, then the **substance forming the cuprotype image** cannot be exactly identical to Hatchett's Brown.

Library Angels

"Library angel" is the term coined by journalist and writer **Arthur Koestler** to describe those mysterious coincidences that occasionally aid researchers—the serendipitous discovery of the right piece of information at precisely the right time.

The author was fortunate to come across *The Chemistry of Cyanogen Compound*s by **H. E. Williams (1915)**, which includes a detailed section on **copper ferrocyanides.**

Consistent with Bersch (1901) and Mayer (1908), the book confirms that insoluble double salts such as **cupric potassium ferrocyanide ($CuK_2[Fe(CN)_6]$)** can be prepared by adding a soluble copper salt (chloride, nitrate, or sulfate) to a large excess of soluble ferrocyanide, preferably in the presence of **the corresponding metal chloride**[53] (in this case, potassium chloride).

Williams explains that **alkali ferrocyanides** (e.g., potassium ferrocyanide) have a far greater tendency to combine with **heavy-metal compounds** of the same type than do the **alkaline-earth salts** such as calcium ferrocyanide.

Copper(II) dipotassium hexacyanoferrate(II)
$CuK_2[Fe(CN)_6)]$
Synonyms:
Cupric potassium ferrocyanide
Cuprous potassium ferrocyanide
Copper–potassium ferricyanide

Fig. 1.7 — Potassium copper ferrocyanide is a compound associated with Hatchett's pigment, yet chemically distinct from it.

Approximately

From the tangle of gathered documents, the two ends of the thread finally emerge: the color is very similar, yet the structure of the filament is different.
There is, therefore, a "knot" that ties together two things which, in reality, have distinct origins. The first end is **Hatchett's pigment**, the second is **the cuprotype pigment**; the junction was made (in good faith) during the nineteenth century, when the pigment devised by the English chemist began to be employed in the traditional art of making paints and varnishes.

Just as a varnish—whose very purpose is to conceal the substrate of a material, giving it the color and appearance of something it is not—contains within it ancient practices and arcane conventions despite the many impulses it has received from modern scientific disciplines such as chemistry,[59] it is not surprising that the art of making colors may also obscure the true origins of certain materials.

Essentially, and for practical reasons, **two different substances** were historically associated under a single pigment name.

There was no intent to deceive, nor is this an isolated case. One might recall, for instance, the famous Prussian blue, much loved by practitioners of historic photographic techniques: the pure pigment—composed solely of ferric ferrocyanide—cannot be obtained through classical cyanotype. That process yields a compound that also contains **potassium** (see Chapter VI), which is almost identical to the "true" Prussian blue but chemically distinct.

In essence, a family of related compounds exists within this group of blue pigments.
By the same reasoning, one may say that the **cuprotype process cannot yield the pure red-brown pigment composed of copper(II) ferrocyanide**, though it can produce compounds that belong to the same family and represent a close variant.

To summarize:

- **Hatchett's Brown** is a pigment composed of pure copper(II) ferrocyanide, obtainable only through a specific synthesis.

- **The cuprotype process** cannot produce pure copper(II) ferrocyanide—completely free of potassium.

> Having established this distinction, from this point forward the term Hatchett's Brown will no longer be directly associated with cuprotype printing.
> For the sake of brevity—and to avoid repetitive technical clarifications—the term **copper(II) ferrocyanide** will be used in a general sense, referring specifically to **potassium copper ferrocyanide** or **ammine copper ferrocyanide** as formed in photographic printing processes.

II

The Patterson Process

Page 40: *Inner Conditions (Spleen)*
Cuprotype print, Patterson process (modified), on Fabriano Unica paper (250 g/m²)

The Work Area

Practicing the **cuprotype** does not require a photographic darkroom or any other space with safelight illumination. The relatively low photosensitivity of the compounds and coated papers allows work to be carried out in any space where the light can be suitably dimmed.

The **sensitizing solution**, both before and after being applied to the paper, is **photoactivated**, especially by **ultraviolet and/or blue light**.
Shutters and curtains are therefore sufficient to create a temporary protected environment, shielding the workspace from direct sunlight.

If **artificial lighting** is needed, a **low-power incandescent bulb (40W)**[1] is preferable. Most of the radiation emitted by a tungsten-filament lamp lies within the "safe" portion of the electromagnetic spectrum, provided that work is done at least **two meters** away from the light source.

Work surfaces should be **flat, stable, clean**, and **free of unnecessary objects**.
Setting up all tools and materials in the correct working order before beginning the printing session is an excellent way to prevent mistakes—something always possible in **small or dimly lit spaces**.

Having **running water nearby** is essential both for the printing operations and for **safety reasons**.
A **ventilation system** is not strictly required, but it is important that the workspace can be **aired when necessary**. Above all, it is fundamental to maintain simple, clean, and orderly working methods, and to be well informed about the hazards associated with the chemicals (see Appendix III) and the procedures to be followed before beginning any work.[2]

Finally, the **disposal of chemical waste**, both solid and liquid, must be carried out in accordance with **local environmental and safety regulations**.

Warnings and Disclaimer

The practical instructions contained in this text involve the handling of certain **chemical reagents** that are considered **toxic or hazardous**.
The risks associated with the use of these substances are detailed in the **dedicated appendix (pp. 215–232)**.
However, it is the **reader's and practitioner's responsibility** to inform themselves about the **specific risks** of these substances, to take all necessary **precautions**, and to implement all **appropriate safety procedures** when handling them.

Material Safety Data Sheets **(MSDS)** can be consulted online at:
https://sdsmanager.com/us/search/
(You can select the language you prefer.)

The author **declines all responsibility** for any harm, injury, damage, or loss resulting from the use of the chemicals or the procedures described in this text.

It should also be noted that:

- **The quantities of reagents** required for the practices described in this book are **very small**.
- The **hazard pictograms** displayed on reagent labels refer to the **pure, concentrated substances**.
- The procedures described here make use of **highly diluted solutions**, which means the **risk is considerably reduced** both for the practitioner and for the environment.
- The **fundamental principle** is to remain **aware of one's actions** and to recognize that these materials are **potentially hazardous**—the same applies to **artists' materials** as well as to **household cleaning agents**.
- By adopting **clean, organized, and rational working methods**, combined with the use of **basic personal protective equipment**, the overall level of risk can be **further minimized**.

The Patterson Process

> This chapter describes the key procedures that provide a sufficiently broad overview of the cuprotype printing process.
> Patterson's reworking of Obernetter's original formula serves as both a historical and technical foundation for understanding the modifications introduced by the author of this text to refine the technique.

Patterson's recipe is available from various on-line sources, though the information is not always consistent or clearly presented.
It is a formula suitable for contact printing that yields low-contrast prints with moderate to low density, starting from a negative of standard density and tonal balance.

Optical Density

When referring to the density of an image, the term denotes its optical density, either maximum (D-max) or minimum (D-min).
In densitometry, optical density corresponds to the degree of darkness in a developed or printed image. It may be expressed:

- Absolutely, as the number of opaque particles (e.g., silver grains in photographic film) per unit area, or
- Relatively, as a numerical value on a logarithmic scale.

Optical density is measured by the reduction in light transmission through a transparent medium—essentially, the light absorption of the material. The corresponding instrument is called a densitometer (or absorptiometer). Thus:

- D-max = maximum achievable optical density
- D-min = minimum achievable optical density

The density range of a material corresponds to its exposure range or dynamic range—the range of light intensities that can be faithfully reproduced.[3]

Process Overview

1. Preparation of the photosensitive solution and other chemical baths for print processing
2. Coating the paper support with the sensitizing solution.
3. Drying the coated paper
4. Exposure of the sensitized sheet to a UV light source (bromograph, UV lamp, or direct sunlight)
5. Chemical developing/fixing of the print
6. Clarification bath, removing residual iron salts
7. Toning bath, forming the characteristic red-brown pigment of the cuprotype
8. Final wash to remove chemical residues
9. Drying of the finished print

Preparation of the Working Solutions

Required equipment for preparing the Patterson process solutions:

Table 2.1

Technical Material	Quantity
200 mL Pyrex glass beaker	1
100 mL Graduated cylinder	1
Glass stirring rod	1
100 mL Dark glass or PET bottle	1
1 L Glass or PET measuring jug	3
Precision scale (decimal reading)	1

Fig. 2.1 — Glassware for the preparation of the sensitizing solution.

Fig. 2.2 — Trays and accessories for print processing.

The Sensitizer

The photosensitive (or sensitizing) solution consists of a single mixture made from two reagents dissolved in water: iron(III) ammonium citrate as the light-sensitive agent and copper(II) sulfate as the copper source.

Table 2.2

Chemicals	Quantity
Copper(II) sulfate pentahydrate	12 g
Iron(III) ammonium citrate (green type)	12 g
Purified/distilled water (to make up to)	100 mL
Tween ® 20, 20% v/v solution (optional)	1 mL

Fig. 2.3 — From left: Ferric ammonium citrate (green type) and copper(II) sulfate pentahydrate.

Purified water is demineralized water, meaning it is free of the naturally dissolved mineral salts that could otherwise lead to the formation of insoluble compounds (mainly carbonates) in the sensitizing solution, which would reduce its effectiveness.

Tween ® 20 (Polysorbate 20) is a non-ionic surfactant with a neutral pH. In alternative photographic printing, it is used for its ability to form solutions with high emulsifying and solubilizing properties.

The cuprotype sensitizer has limited ability to be absorbed by paper fibers; adding Tween® 20 reduces its graininess and lowers surface tension, helping it penetrate the paper more effectively.

The proper amount depends on the specific porosity of the chosen paper. A 20% solution of Tween® 20 is prepared, and one drop is added for every 10–15 mL of sensitizer. It is recommended not to exceed this amount.

The following procedure involves the use of a **light-sensitive chemical reagent**, ferric ammonium citrate—therefore, all operations must be carried out **under dim light conditions.**

Preparation

In a 200 mL beaker (or another suitable container of equivalent characteristics and volume), pour about **70 mL of purified water** at room temperature.

- Add **12 g of copper(II) sulfate pentahydrate** and stir the liquid until the salt is completely dissolved. To make the process easier, the water can be gently warmed to about **30–35 °C**.
- Then add **12 g of ferric ammonium citrate (green type)** to the solution (see Fig. 2.4) and stir until fully dissolved.

Iron(III) ammonium citrate
$(C_6H_4O_7) \cdot xFe^{3+} \cdot yNH_3$
Synonyms:
Ferric ammonium citrate
Ammonium ferric citrate
E 381b (Food supplement)

Note on the images

The photographs illustrating this process are **for demonstration purposes only**.

The photosensitive material **must not be handled in full light**.

Copper(II) sulfate pentahydrate
$CuSO_4 \cdot 5H_2O$
Synonyms:
Cupric sulfate (pentahydrate)
Copper sulfate (pentahydrate)
Copper(II) sulfate (hydrate)

Fig. 2.4 — After completely dissolving the copper sulfate in water, add the ferric ammonium citrate (green type) to the solution.

- Bring the final solution to a total **volume of 100 mL** by adding purified water (Fig. 2.5).

Fig. 2.5 — The solution is brought to a final volume of 100 mL by adding more purified water.

The sensitizing solution should appear as a **clear, dark green liquid**.
Store this solution in a dark glass bottle (Fig. 2.6) and keep it in a cool, dry place, **away from direct light and heat sources**.

Fig. 2.6 — The photosensitive solution should be stored in a dark bottle, protected from direct light and heat.

In particular, Patterson's sensitizer is **unstable above pH 8**, where copper and citrate ions react to form practically **insoluble copper citrate precipitates**.

Similarly, the **calcium carbonate** found in archival papers (ISO 9706 and ISO 11108) can degrade the image unless removed by pre-treatment.

Suitable papers for cuprotype:

- 100% **alpha-cellulose** or **natural plant fibers** (e.g., cotton, bamboo)
- **No alkaline buffering**
- **No surface sizing**
- **Acid-free**, and without **optical brighteners**

Fig. 2.9 — The papers most popular among practitioners of historic photographic techniques are 100% cotton fiber, unsized, non-alkaline, and acid-free.

Smooth, heavy papers (160–300 g/m²) are preferred for their strength and even absorption.

Grammage (paper weight) is defined as the ratio between a sheet's weight in grams and its area in square meters, expressed as g/m².

Preferred characteristics:

- Resistant to wet processing, abrasion, and tearing
- Weight: between 220 and 300 g/m²
- Smooth (non-laid) surface

The Brush

The sensitizer can be applied to the paper support in various ways and with different tools, the most common of which is the **flat brush**; only this method will be discussed here.

The market offers a wide range of products suitable for the practice of alternative photographic printing processes, which can be easily found in most art supply stores.

Fig. 2.10 — From left to right: Hake brushes with goat-hair bristles, a synthetic-bristle brush with a plastic ferrule, and fine synthetic-bristle brushes with stainless steel ferrules.

Fine synthetic bristles are an excellent alternative to natural hair: they have comparable absorbency, greater durability, and allow for a smoother, more controlled application of the sensitizer.

A **flat**, **short-bristle brush** provides **greater precision and control**, ensuring **even coating** while minimizing waste of the sensitizing solution.
The bristles—whether **natural or synthetic**—must be **soft,** to avoid damaging the paper surface.
Scratches or abrasions not only mar the aesthetic appearance but also cause **uneven absorption**, resulting in **localized density variations** in the print.

The sensitizer must not come into contact with **metals**, as any **oxidized residue** could contaminate it; therefore, brushes with **plastic** or **stainless-steel ferrules** are recommended. Many experts suggest using brushes whose bristles are bound with thread or cord and **contain no metal parts.** In the practice of historical printing techniques, **string-tied or cord-bound Hake brushes**—flat, with soft **goat** or **camel hair bristles**—are particularly popular.

A good brush should:

1. Have **high-quality bristles**;
2. Be **used properly**;
3. Be **cleaned and stored carefully**.

Following these three simple guidelines is often enough to ensure **excellent results**, regardless of the brush type.

Preparing the Support: Coating

☞ **Operation to be carried out under dim light conditions**

The procedure aimed at creating a uniform layer of sensitizer on the printing support is called **coating**.

Taking into account the size of the negative, and marking (if necessary) the area of the paper to be printed, that area should be evenly coated with the sensitizer, extending beyond the image borders—as much as personal preference dictates.
Before the first application, the dry bristles of the brush should be **dampened with purified water** to prevent them from absorbing too much sensitizer; the excess water is then **blotted off with absorbent paper** (Fig. 2.13).

Fig. 2.12 — Equipment required for the first stage of the cuprotype printing process: coating the paper with the sensitizer.

Fig. 2.13 — The brush bristles should be dampened before coating; excess water is blotted off with absorbent paper.

The **amount of sensitizer** needed for coating a sheet varies depending on the **type of paper.** Too thin a layer will lack sufficient pigment-forming material, while too thick a one will result in **uneven image density**, caused by **non-uniform drying**.

For consistent results—especially when producing a series of prints—it is important to **always use the same quantity of sensitizer,** as this ensures **standardized output.**[8]

Determining the exact quantity of sensitizer is difficult.
Each paper interacts with the sensitizer differently, and its absorption is influenced by ambient factors such as humidity and temperature.

As a general rule, for an **ISO A4 sheet (21 × 29.7 cm)**, a volume between **2 and 4 mL** of sensitizer is a good estimate (slightly in excess).
Taking the average value of **3 mL** as a reference, the approximate quantities are:

Table 2.6

ISO	A5	A4	A3	A2
cm	14.8 × 21	21 × 29.7	29.7 × 42	42 × 59.4
in	5.8 × 8.3	8.3 × 11.7	11.7 × 16.5	16.5 × 23.4
mL	1,5	3	6	12

Once the quantity is determined, proceed in one of the following ways:

1. Using a **pipette or dropper**, measure the appropriate volume of sensitizer and pour it into a **wide, shallow container** (Fig. 2.14). Dip the brush into it and coat the paper evenly.
2. Measure the same amount of sensitizer, pour it **directly onto the center** of the sheet (Fig. 2.15), and spread it uniformly with the brush.

Fig. 2.14 — Left: the sensitizer collected in a beaker and in a Petri dish.

Fig. 2.15 — Standardized results are obtained by always measuring the same amount of sensitizer.

Apply the sensitizer quickly, covering the entire desired area with **slightly overlapping parallel strokes**—first along the **long side** of the sheet (Fig. 2.17), then **perpendicular to it, along the short side** (Fig. 2.18).

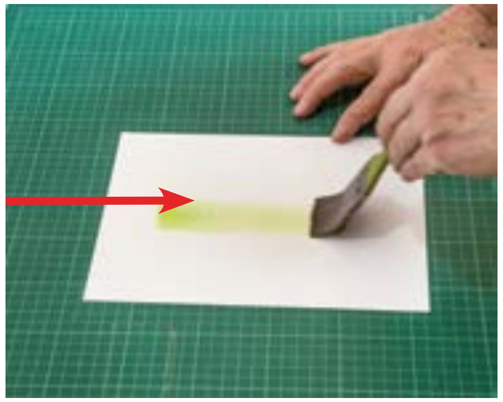


Fig. 2.16 — The sensitizer is first brushed parallel to the long side of the sheet.

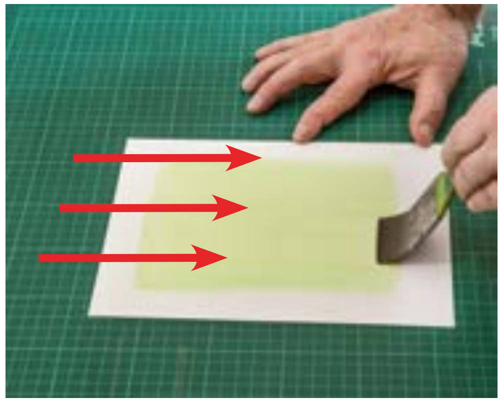


Fig. 2.17 — Continue brushing in the same direction until the entire desired area is evenly covered.

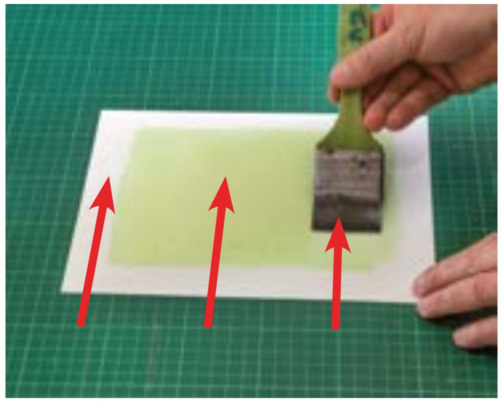


Fig. 2.18 — After coating the sheet uniformly along its long axis, the direction of the brushstrokes can be crossed. Continue brushing in both directions until no liquid pools remain on the paper surface.

Once a continuous and even layer has been achieved, continue more slowly, alternating brushstrokes in both directions, until the paper has **absorbed the liquid** evenly and **no surface pooling remains**.

Drying the Sensitized Sheet

☞ **Operation to be carried out under dim light conditions**

After coating, the sheet should be laid flat on a drying screen or another level, ventilated surface to dry. At this stage, drying must occur under **normal ambient conditions** and should **not be forced**; otherwise, copper sulfate may crystallize on the surface of the paper before properly penetrating it.
When the coating loses its wet sheen, absorption has occurred.

Drying is a simple process that requires minimal intervention but must be monitored carefully. It should **not be accelerated excessively**, although it can be gently assisted by a fan or a hair dryer, provided that it's kept at a safe distance and the heat is not too strong, as excessive warmth can damage the photosensitive layer.

It's equally important that the coated layer not be **completely dry**.
Chemical reactions are facilitated by moisture, which provides the medium that allows them to occur. Without humidity, molecular interactions—and therefore **photoreduction reactions**—cannot take place or spread efficiently.[9]

There's no need for special tools to determine the right level of dryness: the surface should look flat and uniform, not shiny, and should feel dry to the touch.

Once dry, sensitized sheets remain effective for a moderate period. Stored in a dark, not overly dry place, they can be exposed even **after several weeks** without significant quality loss.

Observation of the Transient Image

Once the exposure phase is complete, and the negative film is removed from the surface of the sensitized paper, the effects produced by UV radiation become clearly visible.
On the sheet coated with the sensitizer—selectively shielded by the negative—the trivalent iron present in the areas hit by radiation is **reduced from Fe(III) to Fe(II)**. This reaction is revealed by a **color change** in the sensitized layer: from **light green** it turns **orange**.

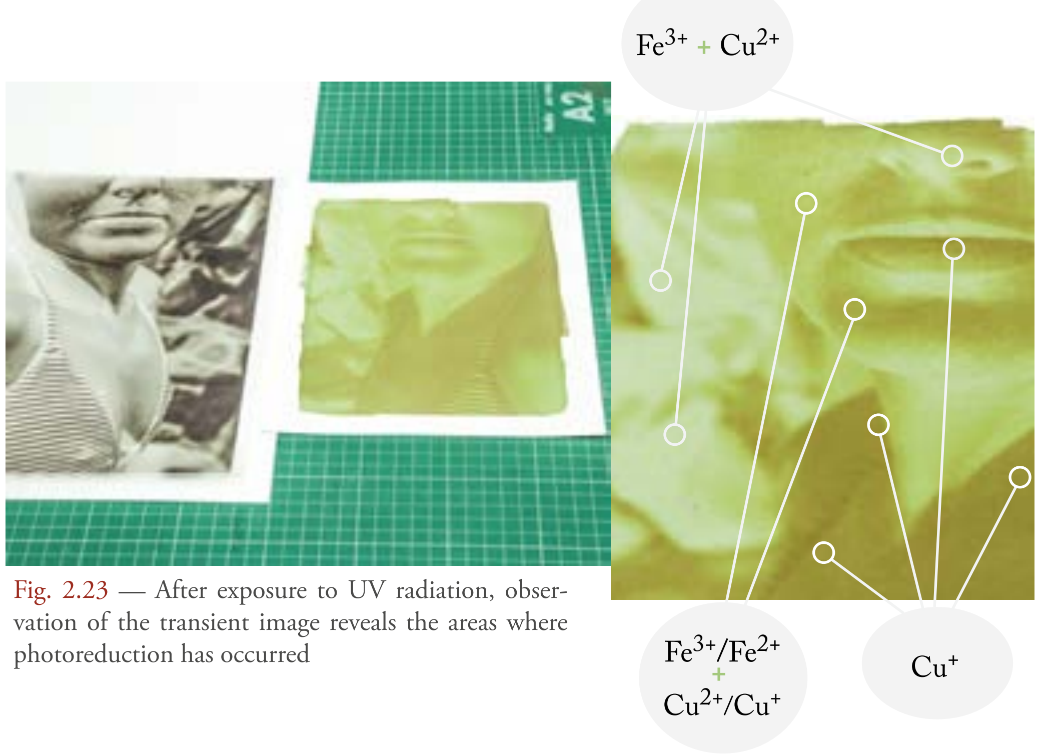


Fig. 2.23 — After exposure to UV radiation, observation of the transient image reveals the areas where photoreduction has occurred

The color remains unchanged in those areas where the denser and darker parts of the negative lay, since they received little or no light.
The **photoreducing action** has instead taken place in the illuminated regions, with greater intensity where more UV light was received.

The image is therefore physically composed of **molecules containing Cu(I)—copper reduced** by the action of ferrous iron Fe(II).
However, its existence is temporary; in order for the image to **become stable and permanent**, it must undergo a **chemical treatment**.

The **iron(II)** obtained through photoreduction is unstable and naturally tends to oxidize back to **iron(III)**. Therefore, sensitized papers can be stored for two or three days before exposure, but it is vitally important that they are **developed immediately after exposure**.

The Chemical Process: Developing and Fixing

As with **cyanotype**, the post-exposure wet treatment serves both to **develop** the image and to **fix** it—that is, to eliminate all compounds that would otherwise continue the photochemical reactions.

> It should be noted that the term *development* is used here in a broad, non-literal sense, since **there is no true development of a latent image**, as occurs in traditional silver-based photography.
> In this case, an image already exists—though still **temporary**—chemically formed by the reduced material.

Table 2.7

Technical / Chemical Material	**Quantity**
Ammonium thiocyanate developer solution (p. 50)	1 L
1 L Glass or PET measuring jug	1
Print tongs	1
Photographic tray (sized to match the print format)	1

Procedure

Table 2.8

Operation	**Method**	**Time** (minutes)
Agitation	Gentle and continuous	2–3

The operation consists of pouring the thiocyanate solution into a photographic tray—using a volume sufficient to cover the paper with about 1–2 cm of liquid.

To prevent the paper, with its dry saline layer, from undergoing stress during immersion—which could damage the image—the operation should be carried out swiftly, followed immediately by gentle agitation.
This is achieved by rhythmically lifting and lowering one edge of the tray, using the opposite side as a pivot (Fig. 2.24).

Agitate slowly and steadily for no more than two to three minutes; continuing beyond that time may result in a loss of image quality.


Fig. 2.24 — One edge of the tray containing the developing solution is tilted upward.


Fig. 2.25 — The print is held ready for immersion.


Fig. 2.26 — The print is slid quickly into the solution while simultaneously lowering the tray.


Fig. 2.27 — The print is gently agitated by rhythmically raising and lowering the tray.

Copper Enters the Scene

The next step is to make the image permanent.
The transient image now begins the first of the chemical treatments that will turn it into a **cuprotype**.

Iron has now completed all of its assigned tasks—it underwent photoreduction and in turn caused the chemical reduction of the key element of this historic photographic technique: copper.

The **ammonium thiocyanate solution** converts all copper atoms reduced during exposure into **copper(I) thiocyanate (CuSCN)** —a stable, water- and alcohol-insoluble copper salt. This compound is gray-white in color, with lilac reflections if impurities are present. It forms and precipitates when a copper(I) compound reacts with a soluble thiocyanate, according to the reaction

$$\mathrm{Cu^{+} + SCN^{-} \longrightarrow CuSCN\downarrow}$$

where **$\mathrm{Cu^{+}}$** is the monovalent copper cation and **$\mathrm{SCN^{-}}$** is the thiocyanate anion. The downward arrow indicates the formation of a solid precipitate.

Cations and Anions

A **cation** is an atom, or a group of atoms, that carries one or more **positive charges** due to the loss of one or more negatively charged particles — **electrons**. It is therefore an ion with a **positive charge**.

An **anion** is an atom, or a group of atoms, that carries one or more **negative charges** due to the gain of one or more **electrons**. It is therefore an ion with a **negative charge**.

The remaining compounds—namely the divalent copper **Cu(II)** and the divalent and trivalent iron **Fe(II)** and **Fe(III)** —are all soluble and are washed away thanks to the action of **citric acid** contained in the composition of this bath.

As mentioned, the **developing/fixing solution** can be reused a few times (two or three), or until the concentration of ferric, ferrous, and cupric salts becomes too high. The accumulation of these salts inevitably leads to problems that drastically reduce the **print quality**.

Fig. 2.28 — The transient image after exposure is composed of reduced copper, over a background of salts unaffected by UV radiation.

Fig. 2.29 — The proto-print after the development–fixing treatment. The image, barely visible, consists of copper(I) thiocyanate, an insoluble salt of whitish-gray color.

The Chemical Process: Clearing the Print

The clearing stage serves to obtain an image with **clean and bright whites**, and it also fulfills another crucial function: **removing iron residue**s still present in the paper fibers.

If this step is not carried out, unwanted bluish stains may appear.
Any residual iron on the paper would react with the **potassium ferricyanide** solution used in the following treatment, resulting in the formation of **Prussian blue**, the pigment characteristic of cyanotype prints.

It is therefore essential that this wash be performed **thoroughly**, always using a **fresh bath**, uncontaminated by residual iron salts from prior use.

Table 2.9

Technical / Chemical Material	Quantity
Clearing solution (p. 51)	1 L
1 L Glass or PET measuring jug	1
Print tongs	1
Photographic tray (sized to match the print format)	1

Procedure

Table 2.10

Operation	Method	Time (minutes)
Agitation	Continuous	3–5

- Pour an appropriate amount of the citric acid–acidified clearing solution into a photographic tray.
- Immerse the print previously treated with the developing/fixing bath.

The clearing bath should last 3–5 minutes.

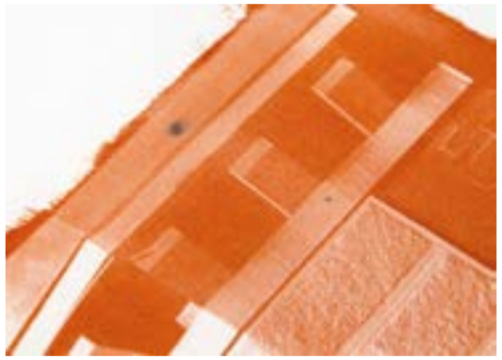


Fig. 2.30 — Bluish stains caused by insufficiently thorough washing.

Fig. 2.31 — The culprit behind these stains is Prussian blue, the pigment of cyanotype.

Toning and Color Shifts

> **Toning**—that is, chemical processes aimed at altering the *hue* or *color* of an image—is generally not favored by the author, except when used for **conservation purposes** to improve the print's long-term durability.
>
> **Copper(II) dipotassium hexacyanoferrate(II)**, the pigment of the **cuprotype**, is inherently very stable and does not require any additional chemical treatment. However, for the sake of completeness and in acknowledgment of **Patterson's** work, his original **toning formulas** are reported below.[14]

Sepia Toner

Table 2.14

Chemicals	Quantity
Distilled (warm) water	1 L
Sodium sulfide	25 g
Selenium powder	5 g

Notes:

- Heat the water and stir until the selenium powder is completely dissolved.
- Store the obtained solution in a **dark glass bottle**.
- **Working dilution**: 1+19 (1 part toner + 19 parts distilled water).

Sepia Toner II

Table 2.15

Chemicals	Quantity
Distilled water	1 L
Rodinal (R09 concentrated developer)	2.5 g
Citric acid	2.5 g

Brown-Violet Toner

Table 2.16

Chemicals	Quantity
Distilled water	1 L
Amidol (2,4-diaminophenol dihydrochloride)	2.5 g
Citric acid	2.5 g

Black Toner

Table 2.17

Chemicals	Quantity
Distilled water	1 L
1,4-phenylenediamine (PPD, black hair dye)	2.5 g
Pyrocatechol (1,2-dihydroxybenzene)	5.0 g
Citric acid	2.5 g

Notes:

- This toner will increase the image density, so it is advisable to start from a slightly underexposed print.
- This toning process also causes the loss of brilliance in the highlights.

The **phenols** present in photographic developers bond with the **cuprotype pigment**, shifting its hue toward **browner, darker tones**; when using these substances, one must accept a **loss in white purity**.
Conversely, **5–10% solutions** of **ferrous** or **ferric salts** (or mixtures thereof) can shift the red tone toward **grayish-blue** hues.[15]

Fig. 2.36 — Original color of an untoned cuprotype.

Fig. 2.37 — Cuprotype toned with amidol — note the loss of white brilliance.

Considerations

After experimenting with the many stages of this **photographic printing process**, a few observations can be made.
Patterson's improvements primarily concern the **sensitizing solution**, while the **chemical treatment** of the print remains essentially identical to **Obernetter's** original method.[16]

The main **advantages** of Patterson's recipe are its **simplicity, low cost**, and **relative effectiveness** of the materials used.
The sensitizer yields images with a **fascinating, antique aesthetic**, though it is not ideal for reproducing images requiring a **high maximum density (D-max)**.
The **low contrast** and **limited density** are intrinsic features of the formula, mainly due to **physical-chemical factors**—notably, the solution's limited ability to penetrate deeply into the paper fibers.

Improvements can be achieved by adding **Tween® 20** or by **pre-treating the paper**. When these adjustments are combined with a **properly calibrated digital negative**, image quality can improve significantly.

Copper(II) sulfate contributes roughly **25% copper by weight** to the sensitizer.
Thus, in 100 mL of a **12% solution**, there are about **3 grams of copper**.
For an A4-sized sheet coated with **2–3 mL** of sensitizer, this provides **0.06–0.09 g of copper**, which is generally sufficient to achieve good density in the shadow areas, provided the copper is effectively reduced by ferrous ions (Fe^{2+}).

However, the **12 grams of ferric ammonium citrate** specified in Patterson's formula appear **insufficient**, due to its **quantum yield** being slightly below **0.5**—meaning that **only half of the Fe(III) ions** that absorb a photon are actually **photoreduced**.[17]

In short, the **iron–copper pair** in this sensitizer cannot supply enough reactive material to produce a **fully dense image**.
One practical solution is the **double coating technique**, applying two layers of sensitizer to increase the available material.

Another factor to consider is the **low light sensitivity** of the solution: its exposure times are **up to 50% longer** than those of a **traditional cyanotype**, and when relying on sunlight, **no practical workaround** can significantly shorten exposure —the chemistry itself must be modified.

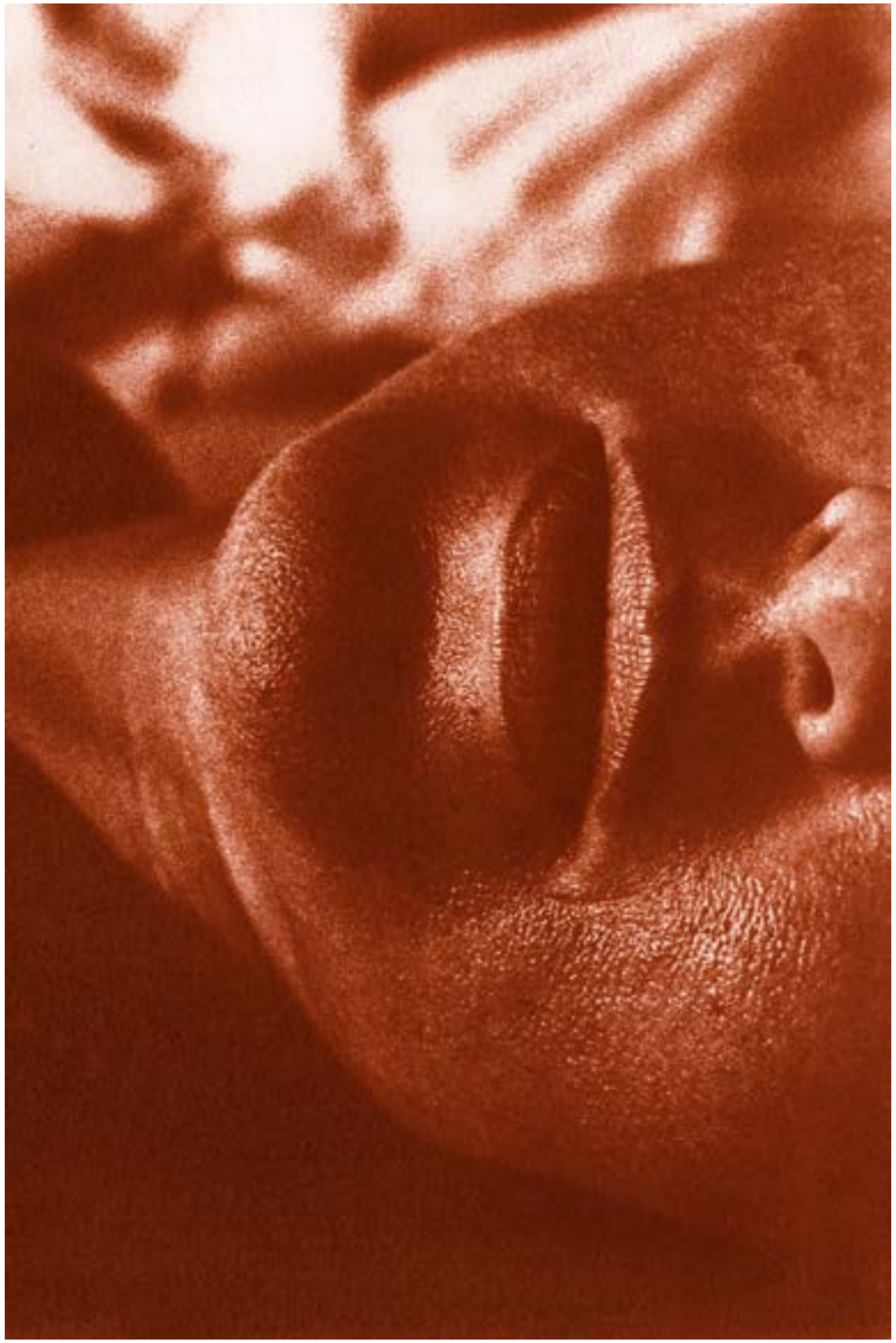
The **rate of Fe(III)** photo-reduction, and therefore the UV exposure time, depends mainly on three factors:

1. The **type of ions** present
2. Their **concentration**
3. The **pH** of the solution.

Studies show[18] that the **optimal photochemical yield** occurs within a **pH range of 1–3**.

Patterson's sensitizer barely meets this threshold (**pH ≈ 3**), but the main limiting factor is the **sulfate ion**, which tends to **inhibit the photolysis of iron**.
This inhibition explains the low efficiency of Patterson's sensitizer, a drawback that the given amount of ferric ammonium citrate cannot overcome.

The **next chapter** will focus on the search for an **alternative sensitizer** to Patterson's, aimed at improving its **less favorable aspects**.



III

An Alternative Solution:
The Carminio Method

In the following table, some comparative data.

Compound	$CuSO_4 \cdot 5H_2O$	$CuCl_2 \cdot 2H_2O$	
Molar Mass (g/mol)	249.68	170.48	
Copper (%)	26.21	38.44	(+46%)
Solubility (g/L, 0°C)	316	706	(+123%)

Table 3.1

When using $CuSO_4$, only the cupric cation Cu^{2+} takes part in the cuprotype reaction, while the sulfate anion SO_4^{2-} has no active role.
In the case of $CuCl_2$, both copper (Cu^{2+}) and chloride ($2Cl^-$) ions take part in the reaction.

Copper is the element that constitutes the substance of the cuprotype: during exposure it undergoes reduction by ferrous iron (Fe^{2+}), thus acting as a **passive subject**.

Chloride, on the other hand, **plays an active role** and contributes to the photochemical process—it **acts as an accelerator**, shortening the exposure time needed for UV light to impress the image.
The simple substitution of sulfate with chloride provides these advantages:

1. A molecule **richer in copper** can promote the printing of denser images.
2. The more than **double solubility** of copper chloride produces a more fluid sensitizer, allowing **better penetration** into the paper fibers and a smoother, more even coating.
3. The combined presence of ferric ammonium citrate and chloride ions enhances the rate of photoreduction, improving yield and **reducing UV exposure times** by at least 50%.

It is worth nothing that replacing ferric ammonium citrate with more photographically efficient compounds such as ferric oxalate or ferric ammonium oxalate, as already noted by Patterson,[3] is not chemically practical since these ferric salts form insoluble compounds with copper—a circumstance that hinders the proper application of the sensitizer.

A New Sensitizer: The Carminio Formula

Once the choice of compounds has been made, the next step is to determine the most suitable quantities.

> In developing the new sensitizing solution, an empirical approach was followed through testing, based on experience gained with other iron-based printing processes (*siderotypes*).

Regardless of the specific siderotype, a 12% concentration of the ferric photosensitive salt—such as that used by Patterson—is insufficient to produce photographic prints with good image density. Under normal conditions, at least twice that concentration would be required.

In the case of cuprotype, now that a more soluble copper source is available, the concentration of ferric ammonium citrate capable of reducing most of the available copper must exceed 30%.
Tests have shown that the ideal concentrations for the reagents are:

- **Solution A**: Ferric ammonium citrate—53% (2M)
- **Solution B**: Copper(II) chloride dihydrate—17% (1M)

The two solutions may be combined into a single sensitizer or kept separate, to be mixed only at the time of use. In the latter case, the general mixing ratio is **1+1**; however, as will be discussed later, there are cases in which it may be advantageous to use different ratios, which is why keeping the two solutions separate may be the more advantageous option.

The greater versatility of the separate solutions, however, comes at the cost of a shorter shelf life for Solution A.
The ferric ammonium citrate solution tends to develop mold on its surface after one or two weeks from preparation, a clear sign of degradation.

This issue, however, can be easily solved by combining the two into a single sensitizer (A+B), ensuring a shelf life of at least two years. Copper salts have strong antifungal properties: both chloride (and the sulfate used by Patterson) create a chemical-physical environment that prevents ferric ammonium citrate from developing mold.

Preparation of the New Sensitizer

Required materials:

Table 3.2

Technical Equipment	Quantity
100 mL beaker	2
100 mL graduated cylinder	1
Glass stirring rod	1
100 mL dark glass or PET bottle	2
250 mL dark glass or PET bottle	1
Precision scale (decimal reading)	1

Table 3.3

Chemicals	Quantity
Iron(III) ammonium citrate (green)	53 g
Copper(II) chloride dihydrate	17 g
Purified/distilled water (to make up to)	200 mL

Operation to be carried out under dim light conditions

Preparation of Solution A

In a 100 mL beaker, pour about 70 mL of purified water at room temperature.

- Add **53 g of ferric ammonium citrate** and stir until the ferric salt is completely dissolved.
- Add purified water to bring the total volume to **100 mL**.

This solution should be stored in a **dark bottle**, in a suitable place, away from direct light, and heat sources.

Fig. 3.2 — Ferric ammonium citrate is a highly soluble salt. When added to water in powder form, it may initially form large clumps, which readily dissolve upon stirring.
To ensure complete dissolution and prevent aggregation, the substance should be added gradually to water while stirring continuously.

Preparation of Solution B

In a 100 mL beaker, pour about 70 mL of purified water at room temperature.

- Add **17 g of copper(II) chloride dihydrate** and stir until the copper salt is completely dissolved.
- Then bring the final solution to a total volume of **100 mL** by adding purified water.

Fig. 3.3 — Copper(II) chloride is a salt that dissolves readily in water; only brief stirring is required for complete dissolution.

This solution is quite stable and easy to preserve: whether kept in a dark or clear bottle, it is best stored away from direct light, and heat sources.

Once an even, continuous layer of sensitizer has been obtained, continue more slowly, alternating brush strokes in both directions until the paper has absorbed all the liquid uniformly.

Drying

☞ **Operation to be carried out under dim light conditions**

After coating, place the sheet horizontally on the surface of a drying rack (or another ventilated, flat surface).
This sensitizer performs best with moderate levels of residual moisture; unless in very humid (RH > 90%) or hot environments, no special precautions are necessary. Drying can be accelerated using a fan or a gentle stream of warm air from a hair dryer.

> The author uses a **foldable cabinet with wire shelves**, equipped with a **small electric dehumidifier**, and a **heating unit** fitted with a fan and thermostat.

Once the sensitized sheets are dry, it's best to expose them immediately; however, they remain effective for some time.
Stored in a dark, moderately humid place, sensitized papers can be exposed even after **1–2 days** without noticeable loss of quality.

Exposure

This formulation reduces exposure time **by 50-60%**.
With an equivalent UV light source (30–35 W effective power), the **15–20 minutes** required for Patterson's solution are reduced to **7–10 minutes** with the **Carminio formula**.

To avoid loss of detail and overall degradation of image quality, **do not overexpose**: the most exposed areas should not turn black, as this would indicate the onset of a new oxidative phase of copper, likely caused by chlorine accumulation.

Fig. 3.7 — After exposure, the areas of the photosensitive layer most affected by light appear more gray compared to those made with Patterson's sensitizer. If the lightest areas are black or dark gray, overexposure has occurred.

Developing and Fixing Treatment

The next step is to make the image permanent.
The **thiocyanate–citric acid bath** (10 + 5 g per litre) proposed by Patterson offers a good balance under most conditions. However, since each paper behaves differently, a well-designed development and fixing bath should adapt to the **specific characteristics of the chosen paper**.

The chemical reagents, and the fundamental principle, remain the same, but to better match certain supports the **proportions** have been slightly adjusted.

1) $$\underset{\textit{cuprous cation}}{\mathrm{Cu}^{+}} + \underset{\textit{thiocyanate anion}}{\mathrm{SCN}^{-}} \longrightarrow \underset{\textit{Copper(I) thiocyanate (white solid precipitate)}}{\mathrm{CuSCN}\downarrow}$$

2) $$\underset{\textit{cupric cation}}{\mathrm{Cu}^{2+}} + \underset{\textit{thiocyanate anion}}{2\mathrm{SCN}^{-}} \longrightarrow \underset{\textit{Copper(II) thiocyanate (black solid precipitate)}}{\mathrm{Cu(SCN)}_2\downarrow}$$

The formation of the **second compound** must be absolutely avoided.
This black, insoluble salt decomposes in humid air, once again forming **copper(I) thiocyanate**.
If this reaction is not prevented, the black salt will deposit both in the **light-exposed** and **unexposed** areas of the image.
This results in the darkening of the highlights and midtones with a corresponding **loss of contrast and detail**.

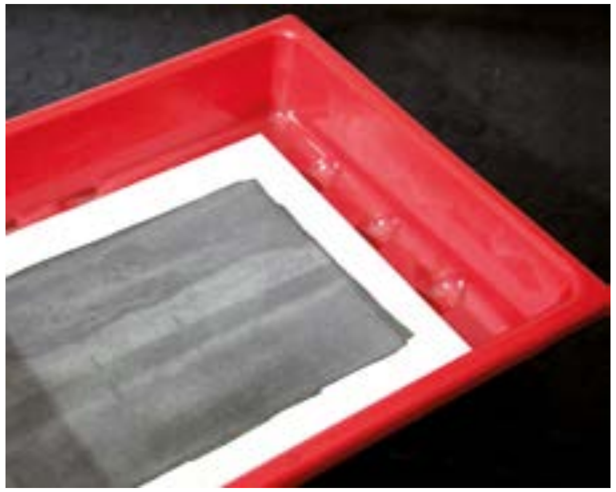


Fig. 3.7 — Proto-print obtained using a sensitizer with an imbalance between the copper supply and the photosensitive compound.
A negative image is created: the dark areas consist of copper(II) thiocyanate, and the light areas of copper(I) thiocyanate.
Exposure to humid air decomposes the former into the latter, almost completely erasing fine detail.
The final print appears dense in the shadows but, due to the total absence of highlights, almost entirely lacking contrast.

That is why the amount of **copper(II)** in the sensitizer must not be unnecessarily or excessively increased if the photochemical system cannot "consume" it—that is, reduce it to **copper(I)**.
In aqueous solution, **copper(II) thiocyanate** forms through the reaction between the **thiocyanate anion** (SCN^-) and the **cupric cation** (Cu^{2+}) when the latter is in excess.

In cuprotype, this occurs mainly when:

- the sensitizer formulation is unbalanced, with an excess of copper relative to the photosensitive compound;
- the development/fixing solution has become saturated (see p. 51) with cupric ions from prolonged use;
- the exposure time to UV light is too short.

Clearing

At this stage, the **iron** has fulfilled its role and must be removed.
Any residues remaining within the paper fibers are eliminated, as they may damage the print. It should be noted, however, that this is **not always desirable**, since the residual iron can, in some cases, be exploited to obtain a **denser image,** as discussed in Chapter VI

Table 3.7

Technical / Chemical Material	**Quantity**
Clearing solution (p. 51)	1 L
1 L Glass or PET measuring jug	1
Plastic print tongs	1
Photographic tray (appropriate for print size)	1

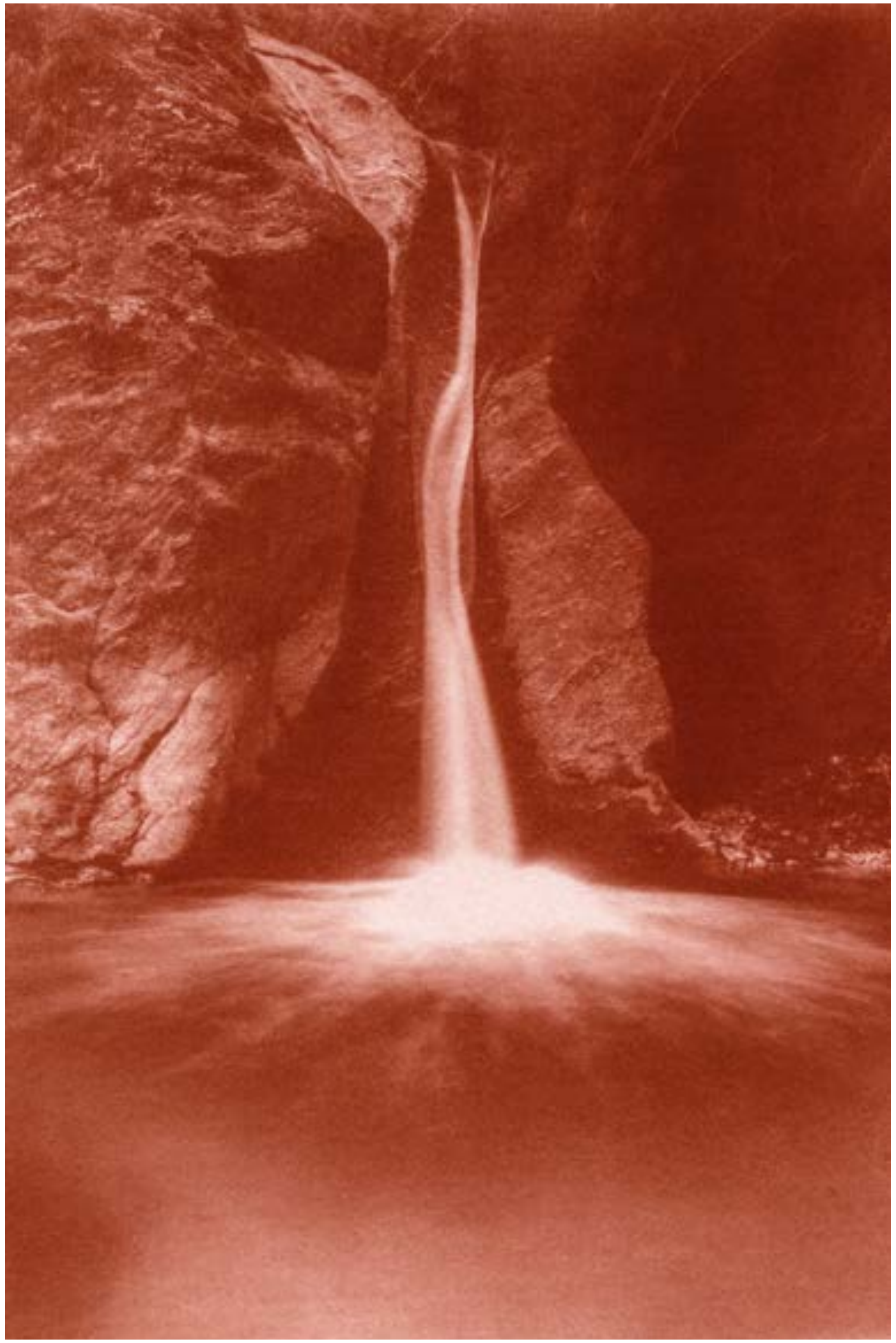
Procedure

Pour an appropriate amount of citric acid–acidified water into a photographic tray and immerse the print previously developed in the ammonium thiocyanate bath. The duration of the bath should be short—one to two minutes at most.

A prolonged clearing bath is generally unnecessary and has no significant drawbacks, as long as the immersion time does not exceed 10 minutes.

Table 3.8

Operation	**Mode**	**Time** (minutes)
Agitation	continuous	1–2



IV

Water!

Fig. 4.4 — Preparation of the iron(III) ammonium citrate solution.

Fig. 4.5 — The copper source is provided by the cupric chloride solution.

- In a smaller beaker, add **9.8 g of ammonium bromide** and dissolve it in about 20 mL of warm purified water.
- While stirring slowly, **pour this solution into the copper(II) chloride solution**: the liquid **turns dark brown** due to the formation of **copper(II) bromide** (Fig. 4.7).

Fig. 4.6 — Preparation of the ammonium bromide solution: the dissolution of the salt is accompanied by an endothermic reaction — it absorbs energy from the surroundings, causing the solution to cool.

Fig. 4.7 — When the ammonium bromide solution is added to the copper(II) chloride solution, a dark brown liquid containing copper(II) bromide is obtained.

- Purified water is added to the solution containing copper(II) bromide until a final volume of **50 mL** is reached.

Fig. 4.8 — The solution containing copper(II) bromide is then added to the iron(III) ammonium citrate solution and gently stirred to mix.

Fig. 4.9 — The sensitizer solution is brought to a final volume of 100 mL by adding additional purified/distilled water.

Fig. 4.10 — The sensitizer is collected in a dark bottle and stored away from direct sources of light and heat.

- This solution is then combined with the first one—the iron(III) ammonium citrate solution—while stirring continuously for **thirty seconds**.
- Add more purified water to bring the total volume to **100 mL**.

This solution should be stored in a **dark bottle**, protected from direct sources of light and heat.

> This solution is concentrated and ready to use but may be **slightly diluted** to improve paper penetration.
> Mixtures consisting of 9+1 or 8+2 parts of sensitizer and water have proven ideal for achieving good image density.

Process Stages

At this point, the only thing left to do is to proceed with printing a new cuprotype, following all the steps previously described:

- Coating the paper with the photosensitive solution.
- Drying the sensitized sheet.
- Exposing the support to a UV light source (bromograph, UV lamp, or direct sunlight).
- Developing and fixing the image.
- Clarification treatment: removal of residual iron salts.
- Toning treatment: creation of the cuprotype pigment.
- Washing.
- Drying.

Coating and Drying

Operation to be carried out under dim light conditions

Under dim light conditions, spread the bromide solution evenly over the sheet and allow it to dry properly, following the same procedure described on pp. 56–58.

As with the other two sensitizers previously discussed, the **bromide-based** one generally requires only air drying under normal environmental conditions (relative humidity between 60 and 85%).
The initial drying phase should proceed naturally until the sensitizer layer no longer appears wet. Afterwards, the sheet may be exposed to a gentle stream of air from a fan or hair dryer, provided that the heat source is kept at a sufficient distance to prevent damage to the photosensitive layer.

It is **always best to expose the sensitized sheets immediately after drying**, since in particularly humid environments the layer tends to reabsorb moisture from the air.

Fig. 4.11 — Sequence (from left): properly dried sheet, after 15 minutes of exposure, and final print.

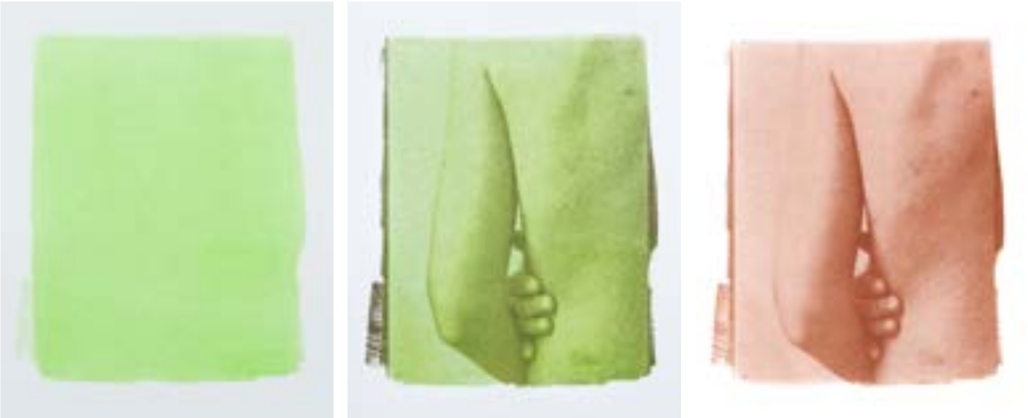


Fig. 4.12 — Sequence (from left): poorly dried sheet, after 15 minutes of exposure, and final print. Residual moisture promotes an oxidative phase during exposure, resulting in prints with low density and contrast.

Printing a negative on a support left too damp will almost certainly produce a poor print, lacking a full tonal range. Indeed, despite appearances, a transient image with overly dark shadows indicates problems related to excessive moisture in the paper and, consequently, in the sensitizer layer coated onto it.

Proper drying, followed by correct exposure, should result in a well-defined provisional image with balanced brightness and contrast levels: **light green** highlights, **orange** midtones, and **orange-brown shadows**.

Exposure

With an effective actinic power of **30–35 W**, this sensitizer requires an exposure time of about **15 minutes**, which may double for dense negatives.
Its relative speed places this sensitizer midway between the Carminio and Patterson formulas.

Exposure time varies with dilution: the more dilute the sensitizer, the **faster** the exposure, but the **lower** the final print density.
A good method for monitoring exposure is to check the darkening of the areas most affected by the actinic light: the darkest parts of the transient image should never turn completely black—this would indicate overexposure, which negatively affects overall image quality.

This issue is also closely related to excess moisture retained by the paper.

Fig. 4.13 — The transient image obtained with the bromide-based photosensitive solution closely resembles that of Patterson's sensitizer, though exposure times are about 20% shorter.

Developing and Fixing

The innovation introduced by this method lies in the use of plain water as both the developing and fixing bath.
Water serves as the medium that allows bromide and cuprous ions to complete the reaction initiated during the exposure stage: they combine to form the **insoluble salt copper(I) bromide,** as previously shown:

$$Cu^{+} + Br^{-} \longrightarrow CuBr\downarrow$$

Nothing else is required for the deposition reaction of the cuprous salt onto the paper to take place. However, adding **10–20 mL** sensitiser solution per litre of water enhances image detail in both highlights and shadows (Figs. 4.14–4.15). This addition should not exceed the recommended amount, since the resulting increase in density affects all areas of the print: highlights gain detail but lose brightness and purity.

Fig. 4.14 — Print developed in plain water. Good contrast and bright highlights, but with little detail.

Fig. 4.15 — Print developed in water plus 10 ml of sensitizer. The increased detail in the highlights is evident.

Technical equipment	Quantity
1 L Glass or PET measuring jug	1
Plastic print tongs	1
Photographic tray (appropriate for print size)	1

Table 4.3

Chemicals	Quantity
Purified/distilled water	1 L
Sensitizer	10–20 mL

Table 4.4

Procedure

In this case as well, Obernetter's working method will be taken as a reference:

- Fill a photographic tray with a suitable amount of the developing and fixing solution, composed of water and sensitizer.
- Quickly immerse the sheet in the bath and agitate gently for about **30 seconds**.
- Then turn the sheet face down, with the image side in contact with the surface of the water, ensuring that no air bubbles remain between the paper and the solution.
- Leave the print to stand (without agitation) for **5 minutes**, taking care to disturb the liquid as little as possible.

Operation	Method	Time (minutes)
Agitation	continuous	0.5
	stand	5

Table 4.5

The action of the water will wash away any visible trace of the image.
Unlike **copper(I) thiocyanate**, which is light gray, **copper(I) bromide** is completely white; its presence on the paper will remain hidden until the toning stage.

Fig. 4.16 — The transient image before development and fixing is a mixture of reduced and unreduced iron and copper salts.
The orange-brown areas correspond to zones rich in reduced copper (Cu^+).

Fig. 4.17 — The proto-print after water-based development and fixing.
The image is now composed of copper(I) bromide, an almost invisible white salt on the paper surface.

Clearing Bath (Clarification)

After development, any residual iron salts must be removed.
This can be done either with **demineralized water** alone or **water slightly acidified** with **citric acid.**

Technical / Chemical Material	Quantity
Clearing solution (p. 51)	1 L
1 L Glass or PET measuring jug	1
Plastic print tongs	1
Photographic tray (appropriate for print size)	1

Table 4.6

Procedure

Pour an appropriate volume of water **acidified** with citric acid into a photographic tray and immerse the print in it. The duration of the treatment should be brief — **30 seconds to one minute at most.**

Operation	Method	Time (minutes)
Agitation	gentle and continuous	0.5–1

Table 4.7

Fig. 4.18 — The color of the image obtained with the bromide method, using the same paper support, is a less intense red compared to the image produced with the Carminio sensitizer. Density and contrast values are low.

Considerations and Comparisons

It is no coincidence that the most widespread alternative printing process worldwide is **cyanotype**, a technique in which the chemical substances involved are kept to a minimum and the steps are essentially two—**exposure** and **development/fixing**—the latter, in its most classic form, involving **only water**.
The simplicity of this process fully justifies its popularity.

There are clear analogies between cyanotype and cuprotype; however, the latter cannot be reduced to such minimal operations—its chemistry does not allow it—although the principles that govern it leave a small margin for adaptation.
A development based exclusively on the action of water has been made possible by exploiting the solubility characteristics of copper bromides.

This, however, is only an *apparent simplification*, since achieving it required making the sensitizer slightly more complex in composition.
Replacing the thiocyanate-based development bath with one composed of plain water has reduced a chemical risk that was already minor, given the low concentration of the salt.

> Nevertheless, it must be remembered that, from a **health and safety** perspective, the main critical aspects of cuprotype are all related to the use of **copper** and are therefore intrinsic to the process itself.
> Copper and its compounds are particularly **harmful to aquatic organisms**, with long-term effects; therefore, special care must be taken to ensure **proper disposal** after use.
> The risk to humans is associated with excessive accumulation in the body, mainly through **accidental ingestion**, for instance, by consuming food or beverages prepared or stored in copper containers.

The photographic performance of this formula differs clearly from that of the other two processes described so far.
The substance that forms the image is visibly **thinner and less dense**, producing **greater brightness** and **lower contrast**.

The proto-print, now consisting of **copper(I) bromide**, is much less affected by the increase in density produced by the ammoniacal ferricyanide toning bath.
This low reactivity results in a longer processing time.

The cause of this, as will be discussed in Chapter VI, lies in the **almost complete absence of ferrous impurities** within the structure of the proto-print, residues inherited from the developing bath, which have a decisive influence on the reactions leading to the formation of the red pigment.

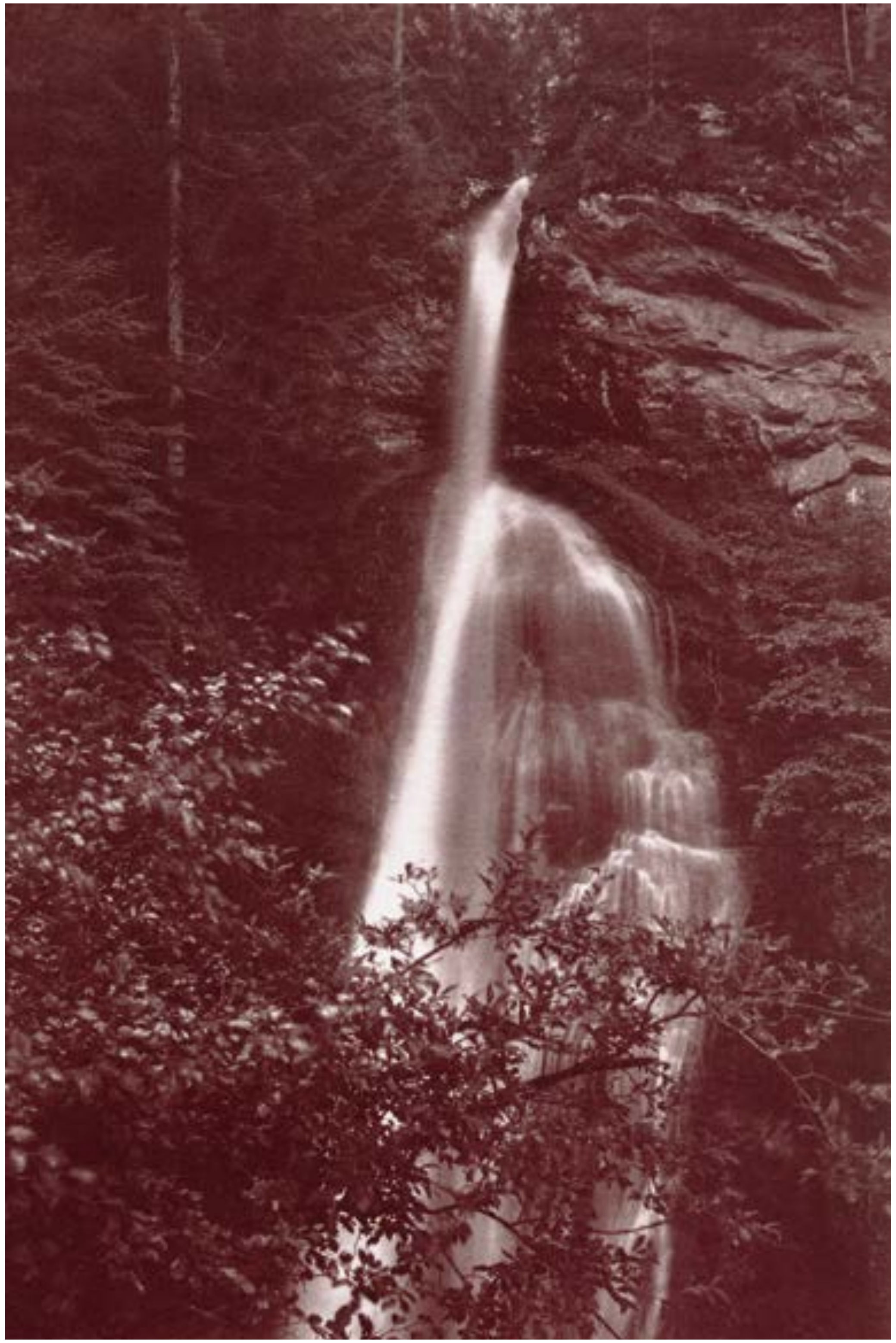
The best results are in fact obtained by adding a few milliliters of the sensitizing solution to the developing water or, alternatively, by introducing a small amount of a **mildly acidic iron salt: ferrous ammonium sulfate (Mohr's salt)** has yielded the most consistent results.

Fig. 4.19 — Prints obtained with the three different sensitizers compared.
From left to right: Patterson, Carminio, and Bromide. The original negative is the same, and the treatments that led to the final prints were carried out under identical conditions, using the same paper.

Other salts may be dissolved in the developing water to increase print density; however, this would contradict the original purpose of the formula: to produce a sensitizer capable of yielding a provisional image **developable in water alone.**

The bromide sensitizer performs best with **negatives of medium density and contrast**; the resulting images are **bright** and display an **acceptable dynamic range**. Due to its nature, it is not well suited for reproducing photographs with **deep shadows**, but, as will be seen later, this apparent limitation can prove an unexpected advantage when the print undergoes toning to alter its **hue**.

Fig. 4.20 — Comparison of density and tone/color:
Bromide process developed in pure demineralized water (top), Bromide process developed in a 0.4% ferrous ammonium sulfate solution (bottom).



V

Obernetter

Even Brown noted a deficiency of ferric chloride and thus proposed increasing it fourfold.

> Brown's suggestion is undoubtedly genuine; however, as will be seen later, the fact that he prepares the toning bath with a **10%** potassium **ferricyanide** solution[7] (rather than **ferrocyanide**, as in the original) indicates only one thing: his source was not Obernetter's original text, but rather **Duchochois's** later interpretation of it.[8]

Fig. 5.1 — Print obtained using Obernetter's iron-cupric process with a brief iron-salt toning treatment. The excess of cupric chloride led to the deposition of a large amount of copper(II) thiocyanate, preventing the formation of pure, bright highlights.

Ambiguities

As mentioned earlier, **Duchochois (1891)**[9] introduced a significant change to Obernetter's original description: in his version, the **toning bath** used **potassium ferricyanide** instead of **potassium ferrocyanide**.

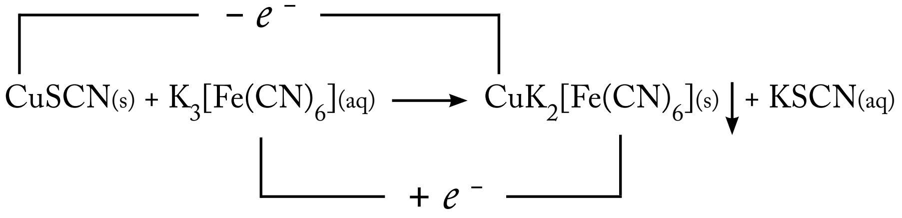
Excluding the possibility of a simple transcription error—though that remains plausible—[10]this substitution has important consequences and, at first glance, appears to be a major improvement: it yields a redder, denser print in a much shorter time than the original recipe.

Potassium ferrocyanide
$K_4[Fe(CN)_6]$
Synonyms:
Potassium hexacyanoferrate(II)
Yellow prussiate

Fig. 5.1 — Potassium ferricyanide (left) and potassium ferrocyanide (right).

In the toning bath, the action of the two different reagents leads to distinct reactions, which, under ideal conditions, ultimately produce the same result.

As previously discussed, in the case of a potassium ferricyanide bath, a **redox reaction** takes place:



$$\overbrace{CuSCN_{(s)} + K_3[Fe(CN)_6]_{(aq)} \longrightarrow CuK_2[Fe(CN)_6]_{(s)}}^{-e^-} \downarrow + KSCN_{(aq)}$$

Ferricyanide **oxidizes** copper, which, by releasing one electron ($-e^-$), changes from monovalent to bivalent: $Cu^+ - e^- \longrightarrow Cu^{2+}$

The ferricyanide anion gains the electron released by copper ($+ e^-$) and is reduced to ferrocyanide: $[Fe(CN)6]^{3-} + e^- \longrightarrow [Fe(CN)6]^{4-}$

In the case of a **ferrocyanide bath**, however, **no redox reaction occurs** in the main phase of the process:

$$2CuSCN_{(s)} + K_4[Fe(CN)_6]_{(aq)} \longrightarrow Cu_2K_2[Fe(CN)_6]_{(s)}\downarrow + 2KSCN_{(aq)}$$

Copper remains in its monovalent state, and **copper(I) potassium ferrocyanide** —or **copper(I) potassium hexacyanoferrate(II)**—is formed.
This compound is an **insoluble**, **colorless** salt[11] when pure, appearing **whitish-pink** if impurities are present.
It slowly oxidizes in moist air[12] to **copper(II) potassium hexacyanoferrate(II)**, which has a **reddish-brown color**:

$$Cu_2K_2[Fe(CN)_6] \xrightarrow{\textit{moist air}} CuK_2[Fe(CN)_6]$$

The End Justifies the Means

Potassium ferricyanide was discovered by **Leopold Gmelin in 1822**,[13] prepared by oxidation of its related ferrocyanide.[14]
By the time Obernetter conducted his ferro-cupric experiments (1863–64), both compounds were well known and widely used.
A question naturally arises as to **why didn't Obernetter, himself a chemist, adopt the ferricyanide**.
The most probable explanation lies in a pragmatic consideration: *"the end justifies the means"*. The goal was **not trying to produce a red image**.

Like **Burnett** before him, his goal was to devise a **chemical photographic process** capable of reproducing the **neutral tones** of silver prints, but without using this precious material, thus providing a **cheaper alternative**.

Only by starting from this essential premise can one understand the technical choices made by these early experimenters.

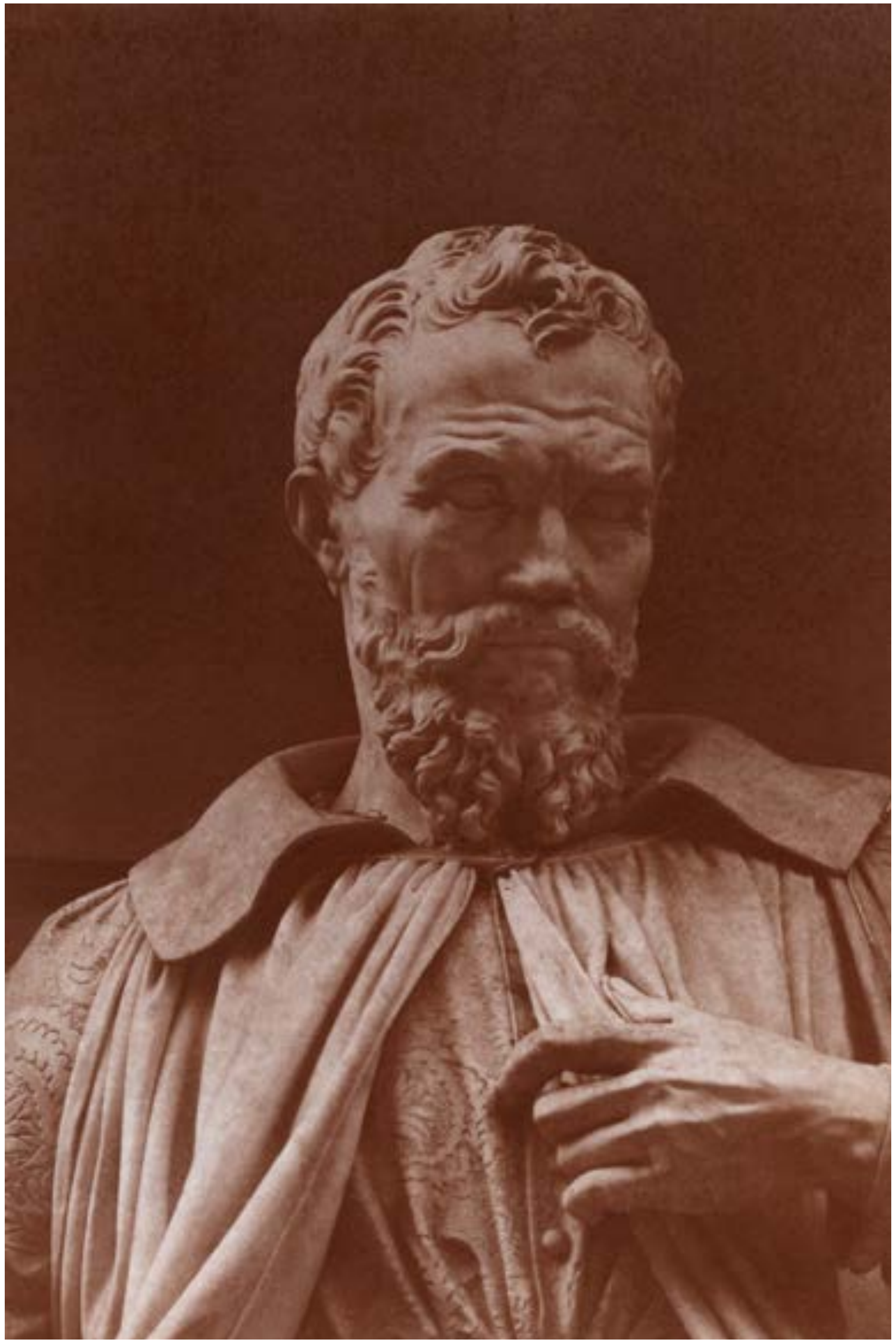
Under identical conditions (same paper, sensitizer, and exposure), a print toned with **ferrocyanide** (Fig. 5.2) closely resembles, in tone and hue, one obtained with **ferricyanide** (Fig. 5.3). The resulting pigment is essentially the same.

However, their image characteristics differ:

- The **ferrocyanide-toned** print offers cleaner details and a broader dynamic range.
- The **ferricyanide-toned** print appears denser, but with lower contrast.

Fig. 5.2 — Print obtained with Patterson's sensitizer and toning in potassium ferrocyanide.

Fig. 5.3 — Print obtained with Patterson's sensitizer and toning in potassium ferricyanide.



VI

The Red and the Blue

Page 148: *Michelangelo*
Cuprotype, Carminio process, on Fabriano Unica paper (250 g/m²).
Toning bath with potassium ferrocyanide (10%), pre-washed with oxidizing bath (hydrogen peroxide 3%, 10 ml/L).

Random Variables

When following the original recipes of historical printing techniques, there is always a **discrepancy** between what one obtains and what one expected (or hoped) to obtain.
Even simply deciphering the quantities of materials can be difficult: the conversion of archaic units of measurement into modern ones is not always straightforward or univocal. One may encounter obsolete nomenclatures that make it difficult to identify the substances involved in a process, together with transcription and translation errors or the authors' occasional "poetic licenses."

The sum of all these variables almost always leads to **unpredictable results**.

Considering that in the case of Obernetter we are dealing with a method that is over **one hundred and sixty years old**, reproducing it coherently is not a matter of following the recipe to the letter, but rather of translating the original conditions into current ones.
Understanding and recreating its "imperfections" is the most difficult task.
Take, for example, the materials themselves: the **purity of a chemical reagen**t produced today is quite different from that of one produced in the mid-19th century. Even the use of a particular procedure for a given treatment can influence the final result, and in this regard it is useful to recall Obernetter's words:

> «The proofs, upon being removed from the water, are placed in a solution of ferrocyanide of potassium, the strength of which may vary between 6 to 12 per 100. In this solution, they assume a red tone, which increases the intensity.»[1]

Under **normal conditions**, one should observe only a faint reddening, since the proto-image—composed of a barely perceptible layer of copper(I) thiocyanate—transforms in the toning bath into an image of **copper(I) potassium hexacyanoferrate(II)**, which is white or colorless (see Figs. 6.1–6.4).

A more pronounced reddening occurs only in the presence of **oxidizing agents**, such as impurities in the water or in the potassium ferrocyanide, or residues in the paper resulting from insufficient washing in previous treatments.

Fig. 6.11 — Print made with Carminio sensitizer after 20 minutes of toning in a 10% potassium ferrocyanide solution.

Fig. 6.12 — Print made with Patterson sensitizer after 20 minutes of toning in a 10% potassium ferrocyanide solution.

Fig. 6.13 — (Carminio) print after 6 minutes of washing in water with 10 ml of 3% hydrogen peroxide added.

Fig. 6.14 — (Patterson) print after 6 minutes of washing in water with 10 ml of 3% hydrogen peroxide added.

Fig. 6.15 — (Carminio) print after final drying.

Fig. 6.16 — (Patterson) print after final drying.

From these images (Figs. 6.11–6.16), one can clearly see the impact of residual iron on image density.

On identical paper supports, prints made with the Patterson sensitizer tend to retain a **greater amount** of iron residues, evidenced by the brownish, rust-like color. These **residues contribute** significantly to **the overall density** of the image at the expense, however, of a slightly **narrower dynamic range** and **less pure highlights**.

The residues left by the Carminio sensitizer are fewer: the resulting print is **less dense** but **more defined** and **luminous**. Tests were also conducted using the **bromide sensitizer**, which produces a proto-image composed of white cuprous bromide. The overall chemistry involved differs, and so do the results.
Copper(I) bromide shows no tendency to retain iron impurities; consequently, this leads to a print that is inherently less dense, but for this very reason, **particularly suitable** for toning. Different methods for different strategies.

Fig. 6.17 — Cuprotype printed with cupric bromide sensitizer, developed in water, and toned with 10% potassium ferrocyanide. The print (of relatively low density) was then toned using Obernetter's ferric salt method and subsequently subjected to a brief bath in 1.5% lead acetate.

The Red and the Blue

The similarities between the molecular structure of the **cyanotype pigment** and that of the **cuprotype** are such that they can be considered analogous compounds[4]. Many of their properties can be understood in terms of the **three-dimensional structure** of the solid at the atomic level; that is, from its **molecular architecture.**

This structure, simple and ideally regular,[5] consists of a **cubic framework** formed, in the case of Prussian blue, by iron atoms alternating between **ferric** and **ferrous** states at the junctions,[6] while in Hatchett's brown, they alternate between cupric and ferrous states. In both cases, the **cyanide groups** (−C≡N−) act as rods, each linking its carbon atom to a ferrous ion and its nitrogen atom to a ferric or cupric one.

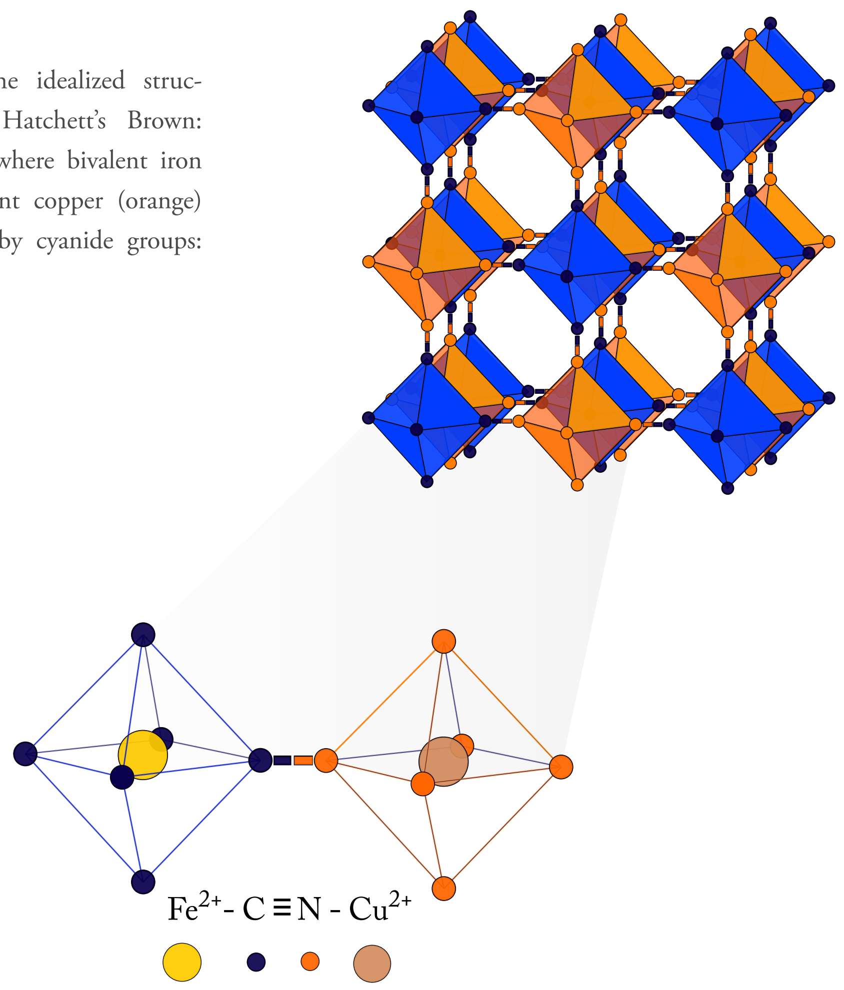


Fig. 6.18 — The idealized structure of "pure" Hatchett's Brown: $Cu_2[Fe(CN)_6]$, where bivalent iron (blue) and bivalent copper (orange) alternate, linked by cyanide groups: Fe^{2+}-CN-Cu^{2+}.

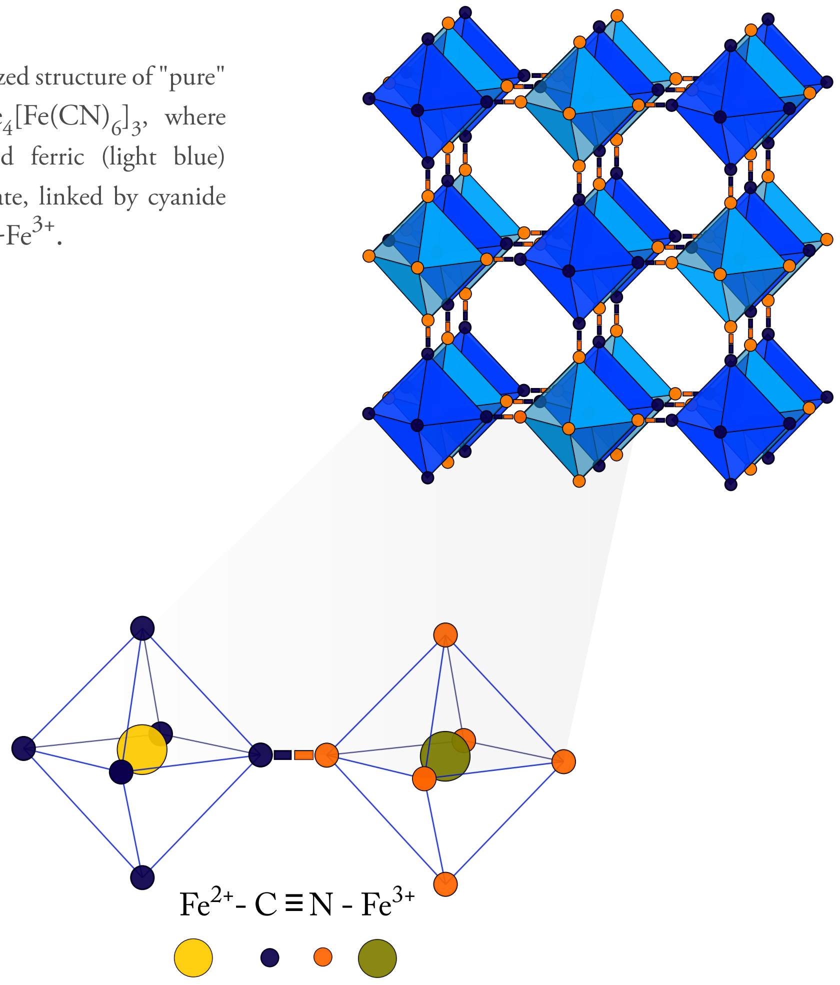
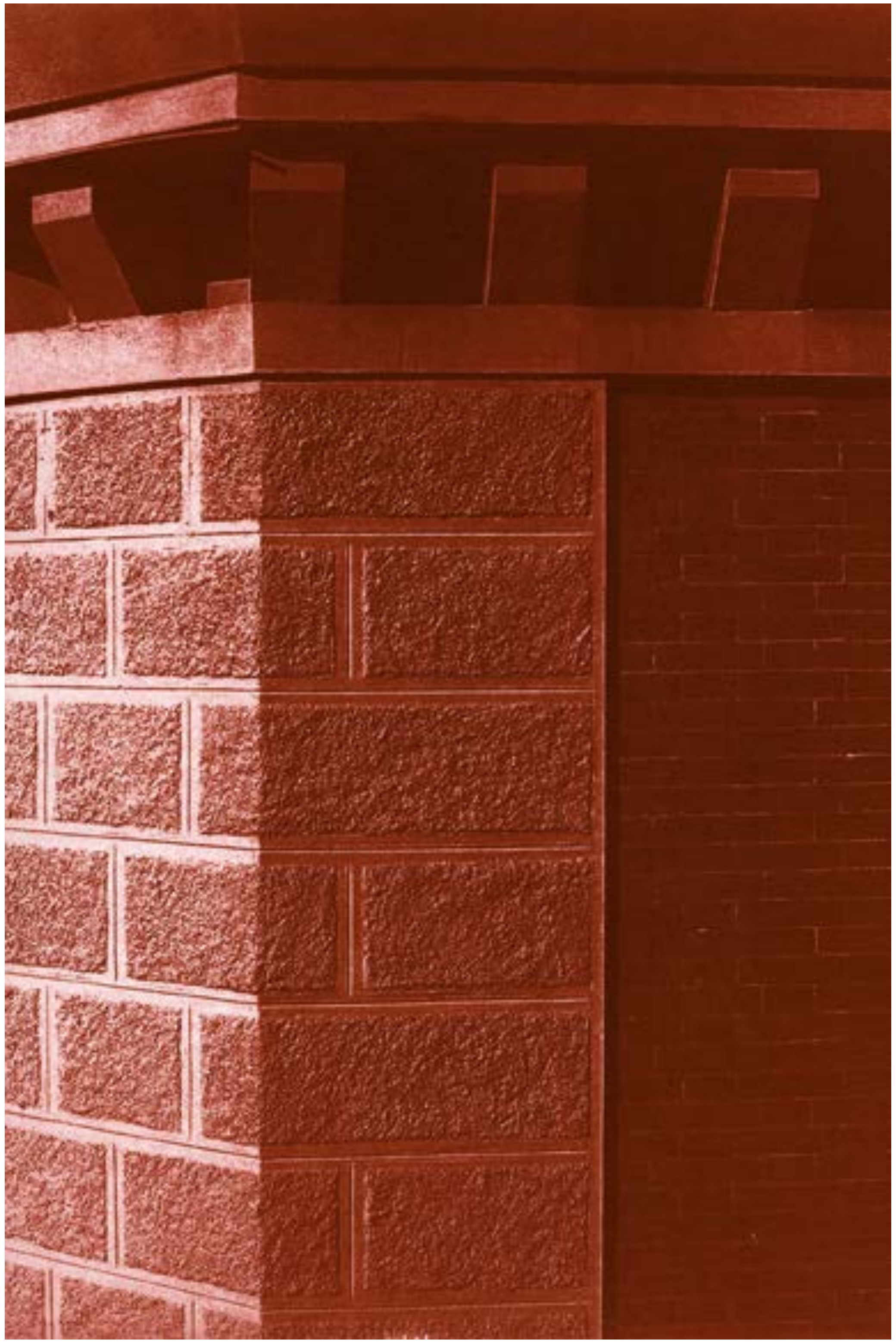


Fig. 6.19 — Idealized structure of "pure" Prussian blue: $Fe_4[Fe(CN)_6]_3$, where ferrous (blue) and ferric (light blue) iron atoms alternate, linked by cyanide groups: Fe^{2+}-CN-Fe^{3+}.

The structure, however, is not compact: it is an open lattice through which run channels extending in three perpendicular directions.
The large cavities inside each cube can host, for example, molecules of water or metallic ions, allowing both compounds to act as *chemical sponges*.

As previously noted, the cuprotype process cannot produce the pigment Hatchett's brown in its pure form: instead, it yields **cupric potassium ferrocyanide,** $CuK_2[Fe(CN)_6]$, where the alkali ions—specifically potassium—fill the empty spaces inside each cubic unit of the molecular lattice.



VII

Another Landscape:
The Hematotype

b) *Prussian blue / Turnbull blue* $\xrightarrow{(+OH^-)}$ *ferric hydroxide*

Although **potassium and ammonium ions** are not mentioned, they are, undoubtedly, present. The reactions summarized above have important implications for the **formation of the ammonium-containing cuprotype pigment** and, consequently, for the fate of these "**silent participants**."

Indeed, the reactions occurring at this stage can be **multiple**, yet they all converge toward the formation of **ferric hydroxide** or, more precisely, of a **precipitated hydrous iron(III) oxide** in the form of a **gel**, which slowly evolves into **more polymerized crystalline forms**.[2]

All of this occurs **in parallel** with the reactions involving **copper**, which lead to the creation of the **ammoniacal cuprotype pigment**: $[Cu(NH_3)_4][CuFe(CN)_6] \cdot H_2O$.

Despite the **complexity of the phenomenon**, it does not seem too bold to assert that **iron plays a supporting yet essential role** in the **cuprotype technique**. Therefore, beginning with **Obernetter**, the definition of the process as **ferro–cupric** is entirely coherent and appropriate.

Another Landscape (From the Shoulders of Giants)

The Patterson method, as well as the Carminio process proposed by the author, revolve around Obernetter's ferro-cupric process, representing its **modern adaptation** and, one might say, its improvement.

As discussed in Chapter VI, each of these sensitizers show a particular **tendency** to leave **iron residue**s within the layer of copper(I) thiocyanate that forms the image of the proto-print; a tendency that varies according to the sensitizing formula used.

After the development process, an operation common to all **siderotypes** is the removal of the iron residues left by the sensitizer, and **cuprotype** is no exception. However, this procedure should be as selective as possible; thorough in the **highlights** of the image (for pure, bright whites) and gradually milder from the **midtones** toward the **darkest areas** (for denser images and deeper shadows).

Today, the photosensitive compounds used in iron-based sensitizers are essentially three: **ferric ammonium citrate, ferric ammonium oxalate, and ferric oxalate** (in some cases also alkaline ferrioxalates). However, for both chemical and physical reasons, contemporary cuprotype practice is generally limited to the use of the first compound.

> In fact, when prepared following a specific method, oxalates can also be used in cuprotype, but this topic will not be explored further in the present text.

Fig. 7.1 — From left: ferric ammonium citrate (green type), ferric ammonium oxalate trihydrate, ferric oxalate hexahydrate.

Using higher concentrations of ferric ammonium citrate is of little help if the goal is to ensure that, during development, a certain amount of iron remains trapped within the structure of the provisional image.

In this regard, the **Carminio process** has probably already reached its theoretical qualitative limit; therefore, it is necessary to look elsewhere, to extend one's view toward a different (chemical) landscape.

From the experiences of the great pioneers of the past, valuable insights can always be drawn, but these alone are not enough. They must be accompanied by a sustained process of reflection and re-elaboration so that specific information can be extracted, reapplied, or, if necessary, discarded in analogous situations.

It is precisely in this spirit that attention will once again turn to Johann Baptist Obernetter's ferro-cupric process.

Fig. 7.4 — Technical and chemical materials for the preparation of the sensitizer.

The proportions of ferric chloride to citric acid are not fixed and can be varied according to the density of the negative.

Good results can be obtained, for example, with a sensitizer composed of **12 g of ferric chloride, 13 g of citric acid monohydrate,** and **17 g of cupric chloride**.

However, this formulation is not suitable for reproducing very dense negatives, where the action of UV light is less pronounced, and the photoreduction of iron is less extensive. In such cases, excess unreduced copper leads to the formation of cupric thiocyanate, which—as previously noted—has a negative effect on the print quality.

Procedure

☞ **Operation to be carried out under dim light conditions**

In a 250 mL beaker (or another suitable container of equivalent characteristics and volume):

- Pour approximately **60 ml of purified water** at room temperature, and dissolve the **citric acid monohydrate** in it; the crystalline compound will dissolve easily with brief stirring.
- To the freshly prepared acidic solution, gradually add **16.2 g of ferric chloride (anhydrous)**, stirring continuously until all solid particles are dissolved. The liquid, initially turbid, should return to a clear, rust brown color; any undissolved residues will be removed later by filtration.

- Add **17 g of cupric chloride dihydrate**, stirring until the salt is completely dissolved.
- Bring the total volume of the solution to **100 mL** by adding additional purified water, then let it rest for about one hour.

The final step is **filtration** through a funnel and filter paper to remove any remaining solid particles. The resulting sensitizer should appear as a dark, clear liquid with a green hue. This solution must be stored in a dark bottle (Fig. 7.5) and kept in a suitable place, protected from heat sources and direct light.

> For optimal results, it is advisable to allow the sensitizer solution to **"age" for a few days** before first use. The solution is stable, and, if properly stored, its useful life can extend **beyond two years**.

Fig. 7.5 — The sensitizer: a dark liquid of emerald-green color.

Technical/chemical material	**Quantity**
Developing/fixing solution	1 L
1 L Glass or PET measuring jug	1
Plastic print tongs	1
Photographic tray (appropriate for print size)	1

Table 7.4

Procedure

Proceed exactly as in the Carminio process, using the *stand development* method:

- **Quickly** immerse the sheet in the developing solution and gently agitate it for **20–30 seconds**.
- **Turn the sheet face down,** with the image in contact with the surface of the solution. **Make sure no air bubbles remain between the image and the liquid.**
- Leave the sheet to stand in the solution **without agitation for 5–8 minutes,** taking care not to disturb the liquid during the entire process.

Operation	**Mode**	**Time** (minutes)
Obernetter's method	continuous	0.5
	stand	5–8

Table 7.5

The action of the thiocyanate treatment is identical to that already observed in the *Patterson* and *Carminio* processes; however, its impact on the transient image obtained with the new sensitizer exhibits distinct characteristics.
Upon contact with the solution, the sensitized layer bearing the photo-impressed image immediately turns a **blood red color.** This is caused by the substantial formation of **ferric thiocyanate**[5], or more precisely, by a complex containing ferric and thiocyanate ions[6]. This can be synthetically represented by the reaction:

$$Fe^{3+} + SCN^{-} \rightleftharpoons [Fe(SCN)^{2+}] \rightleftharpoons [Fe(SCN)_2{}^{+}]$$

This compound is highly soluble, and its rapid dissolution is followed by the deposition of **cuprous thiocyanate (CuSCN),** which is insoluble.
The layer deposited on the paper appears visibly darker than usual due to the inevitable inclusion of iron impurities.

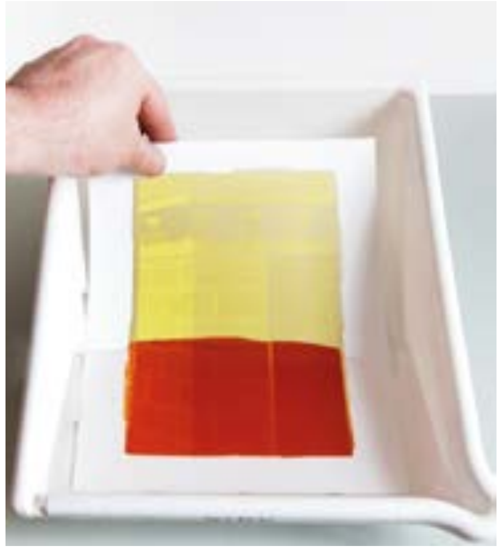


Fig. 7.8 — The sheet bearing the transient image immersed in the developing and fixing solution. Ferric ions react with thiocyanate ions, forming a compound of intense blood-red color.

Fig. 7.9 — The ammonium thiocyanate developing bath before (left) and after (right) treatment of the proto-print. The dark red color of the used solution results from the reaction between ferric and thiocyanate ions.

An Iron-Doped Proto-Print

The choice of ferric chloride as the photosensitive compound has a significant effect on the amount of iron that remains trapped, as an impurity, within the layer of CuSCN that forms the image on the proto-print; a layer that should ideally appear white but instead tends to shift toward a gray-violet tone as the iron content increases.

Fig. 7.10 — Pure cuprous thiocyanate is a chalky solid of very light gray color.

CuSCN has a particular tendency to incorporate impurities within its own structure.[7] In cuprotype printing, this occurs during its deposition onto the paper — the layer that will form the provisional image.

Fig. 7.11 — The proto-print of a cuprotype developed with thiocyanate consists of CuSCN, cuprous thiocyanate, a compound that is virtually white but tends toward gray-violet when iron impurities are present.

Clearing Bath (Clarification)

This is a relatively delicate operation, because it is no longer a matter of removing all the iron from the whole print but only from the areas where the image must appear bright and luminous. Fortunately, the combination of sensitizer and developer solution used in this process naturally yields rather clean highlights, since the iron tends to accumulate only in the areas where CuSCN has been deposited, and in proportion to it: the thicker the deposit, the greater the inclusion of iron.

With this step, a small amount of accumulated iron will be sacrificed but not to the point of significantly reducing the final print density.

It may be carried out in the usual way, using a slightly acidified solution with citric acid, although the author prefers to use a solution of trisodium citrate.

Table 7.6

Chemicals	Quantity
Purified/distilled water (to make up to)	1 L
Trisodium citrate dihydrate	1–5 g

The quantity of citrate to be dissolved should be adjusted according to the paper used; generally, 5 g per litre is the recommended upper limit.

Procedure

Begin with a brief pre-wash:

- Pour plain water into a photographic tray, immerse the proto-print, and agitate gently but continuously for about 30 seconds. Replace the water, and repeat the operation three times.

Table 7.7

Operation	Mode	Time (minutes)	Cycles
Agitation	Continuous	0.5–1	3

At this point, the paper will be sufficiently free of residues from the developing bath, and the proto-print can be treated with the citrate solution:

- Prepare a tray containing the citrate solution, and immerse the sheet.
  In this case as well, the treatment time depends on the type of paper used; stop the process once the light areas appear clear and transparent.

Table 7.8

Operation	Mode	Time (minutes)
Agitation	Continuous	0.5–2

A prolonged clearing bath is generally not recommended, as it may remove too much of the residual iron.
To prevent this, the thiocyanate developer should always be freshly prepared for each session, avoiding an excessive buildup of cupric salts that could lead to the formation of cupric thiocyanate, which is detrimental to print quality.

The duration—ranging from **30 to 60 minutes**—varies according to both the type of paper used and the specific toning treatment applied: **ferricyanide** residues are more persistent than **ferrocyanide**, and cuprotypes prepared with the former require longer washing times. Any unwanted residues, even slight ones, will manifest as **yellowing of the paper**, which can be easily detected by examining the print in transmitted light and under backlighting.

The image density will decrease almost imperceptibly as washing progresses, accompanied by a noticeable color shift whose tone will depend on both the characteristics of the paper and the washing water.

Procedure

Table 7.17

Operation	**Method**	**Time** (minutes)
Washing	Running water	30–60

Drying

After adequate washing and confirming the **absence of potassium ferricyanide/ferrocyanide residues**, proceed with drying.
To avoid excessive stress of the paper, it should be dried horizontally; laid flat on a screen or on another level, well-ventilated surface.

Proper drying is a **slow process** and should take place under controlled, natural ambient conditions. Drying can be accelerated with a fan, but excessive heat sources—including direct sunlight—must be avoided.

Fig. 7.16 — Hematotype obtained using an ammoniacal potassium ferricyanide toning bath.

Fig. 7.17 — Hematotype obtained using a potassium ferrocyanide toning bath. The brown coloration reveals the presence of iron hydroxide formed by the hydrolysis of Prussian blue.

Considerations and Comparisons

There is no doubt that a higher iron content has a significant positive effect on the final print density, and test results clearly demonstrate the difference between the two toning baths.
The **ammoniacal ferricyanide bath** produces prints with very high density and strong contrast, though at the expense of a narrower dynamic range.
The **ferrocyanide toning bath**, followed by a post-treatment oxidizing bath, is a slower process that yields images of slightly greater density but with a wider dynamic range and no significant loss of contrast.
Density, tonal range, and color hue are, of course, also influenced by the type of paper used.

Fig. 7.18 — Above: Hematotype toned with potassium ferrocyanide followed by an oxidizing post-treatment bath. Below: Hematotype toned with ammoniacal potassium ferricyanide. Tests carried out on Fabriano Rosaspina paper (285 g/m^2)

Fig. 7.19 — As in Fig. 7.18, but printed on Fabriano Unica paper (250 g/m^2)

Aside from tone, the best results with the **hematotype** are achieved by making small, targeted adjustments to the **iron-to-citric acid ratio**, fine-tuned to the specific characteristics of the paper employed.

Conclusion

The experimental and practical section of this book was conceived beginning with the **Patterson process**, which, in the author's opinion, represents the only truly coherent and effective reinterpretation of the **historical cuprotype process**.
Starting from this method, the research advanced step by step, eventually leading to the analysis of the **hematotype**, a variant of the cuprotype process that emerged during experimentation.

At the outset of this work, only the **bromo-cuprotype** and the **Carminio processes** had been developed; the hematotype arose in the course of research, combining the distinctive qualities of the Patterson and Carminio methods with those of **Obernetter's ferro–cupric process**.

Throughout the investigation, various interpretative hypotheses were formulated regarding the phenomena characterizing this method—hypotheses that were developed, refined, and eventually tested, while resisting the temptation to adapt data to expectations, only to discover that some proved, at least partially, incorrect. This naturally required a continuous effort of verification and revision.

Some procedures may, therefore, appear contradictory (for example, the cleaning of the proto-print from iron salts, residues that later became fundamental and desirable), but this simply reflects the **progressive and evolutionary nature** of the experimentation.

The hematotype thus represents only a **provisional point of arrival**. Much work remains to be done. First and foremost, verifying its long-term stability and determining whether the **oxidative phase of the pigments** involved continues to progress, which could result in changes in tonal range, hue, and color values.

The exploration of **cuprotype** does not, therefore, conclude with the hematotype. Several alternative experimental directions have shown **promising preliminary results**, though their future development remains uncertain. At present, it is difficult to predict what outcomes may reasonably be achieved yet there remain several **paths worth exploring**.

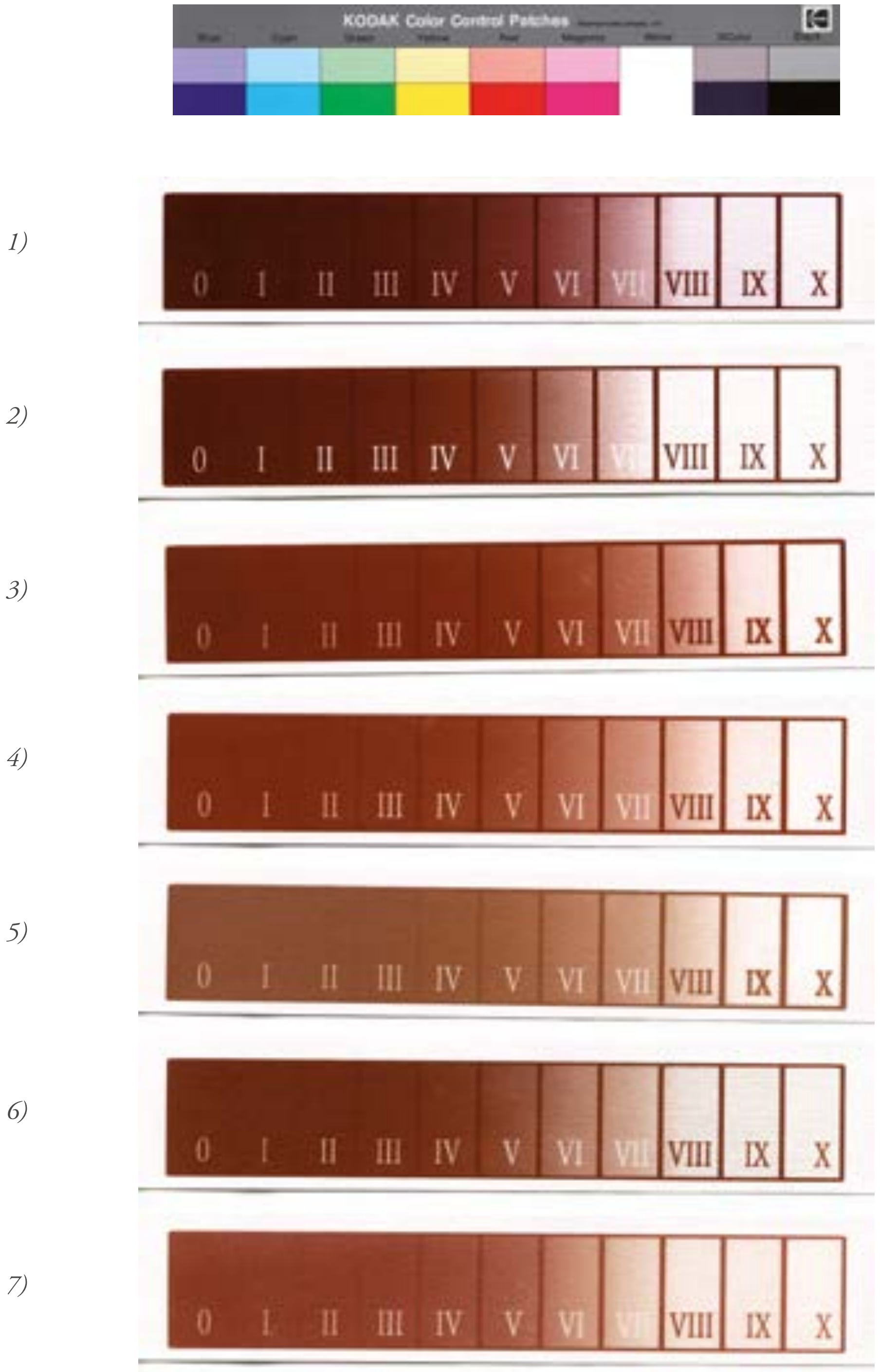


Fig. 7.20 — Scanned color test strips: *1)* Hematotype II, *2)* Hematotype I, *3)* Carminio, *4)* Patterson process with Carminio treatment, *5)* Patterson process, *6)* Bromide process developed with Mohr's salt solution (0.4%), *7)* Bromide process developed with water.

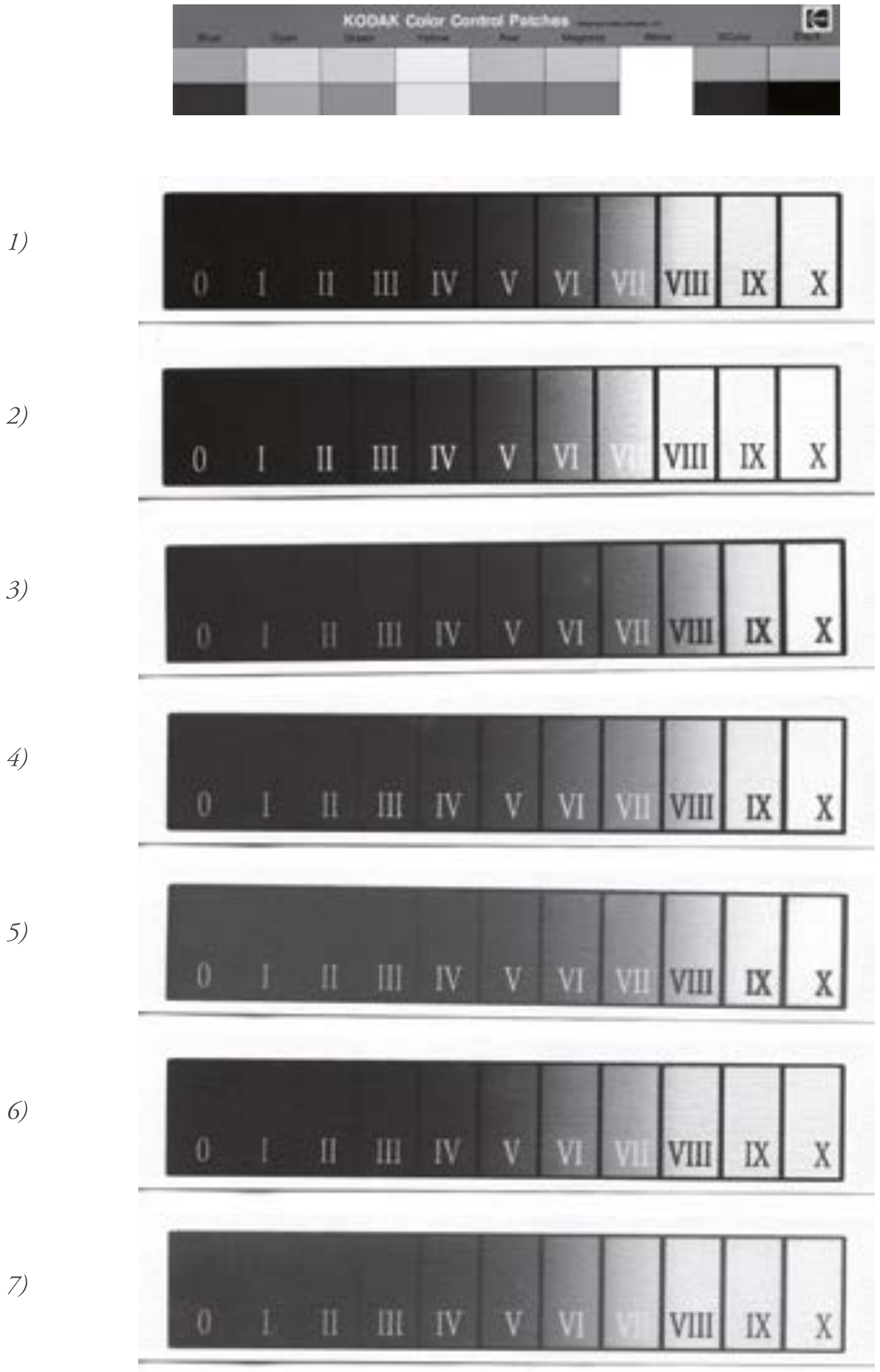


Fig. 7.21 — Scanned grayscale test strips: *1)* Hematotype II, *2)* Hematotype I, *3)* Carminio, *4)* Patterson process with Carminio treatment, *5)* Patterson process, *6)* Bromide process developed with Mohr's salt solution (0.4%), *7)* Bromide process developed with water.

Appendix

I

Cuprotype:

Chronology and Processes

Page 194: *In My Mother's House*
Cuprotype print, Burnett process, on Hahnemühle Platinum Rag paper (300 g/m^2)

Chronology of Copper-Salt Photographic Processes

To propose a **summary chronology of photographic printing processes using copper salts**, one must begin with **Burnett**: the invention of the term *cuprotype* is his, as is the development of the first printing method based on the **chemistry of this metal**.[1] That said, it must be remembered that **Burnett never synthesized his original copper chromate process into a defined formula**,[2] or at least, no documentation of such a formula has ever been found.
The recipe that will be presented here is therefore a partial reconstruction, extrapolated from available sources.
Although it is not, strictly speaking, a **cuprogenic process**, for **historical and philological reasons**, this account will begin with **Robert Hunt's chromatype**, which constitutes the true **origin point** from which **cuprotype** developed.

As for the formula for **cupro-uranotype**,[3] described in **Duchochois's** book—attributed to **C. J. Burnett**, though its chronology and sources remain unclear—because of the **peculiarity of the materials involved** (uranium nitrate), it is preferable to refer directly to the original text:

P. C. Duchochois (1891)
Photographic Reproduction Processes: A Practical Treatise of the Photo-Impressions Without Silver Salts
New York: The Scovill & Adams Company, 423 Broome Street.

The eBook version of the original publication can be **downloaded free of charge** from the ***Project Gutenberg*** virtual library:
<https://www.gutenberg.org/ebooks/24016>

Chromatype,[4] Robert Hunt (1843)

Sensitizer
(1:1 mixing ratio)

Copper(II) sulfate
pentahydrate
12.5 g
Water
(purified/distilled)
100 mL

Potassium dichromate
11.5 g
Water
(purified/distilled)
100 mL

Developing
1–2 minutes

Silver nitrate
8 g
Water (purified/distilled)
100 mL

Fixing
60 minutes

Water (purified/distilled)
(with frequent water changes)

Cuprotype, Burnett Process (1857)

Sensitizer
(1:1 mixing ratio)

Copper(II) sulfate
pentahydrate
10.5 g
Water
(purified/distilled)
100 mL

Potassium dichromate
12 g
Water
(purified/distilled)
100 mL

Developing/fixing
15–30 minutes

☞ **Citric acid**
0.5 g/L
Plain water
(with frequent water changes)

Toning
20–60 minutes

Potassium hexacyanoferrate(II)
(Potassium ferrocyanide)
50–100 g
Water (purified/distilled): **1 L**

Washing
30–60 minutes

Plain water

☞ = optional

Cuprotype, Obernetter's Ferro–cupric Process (1863-64)

Sensitizer

Iron(III) chloride
anhydrous
10–11 g

Hydrochloric acid
concentrated
12 g

Copper(II) chloride
dihydrate
100 g

Water (purified/distilled): **1 L**

Developing/fixing
3–5 minutes

Potassium thiocyanate
8–12 g

Sulfuric acid
1 mL

Sensitizer
10–20 mL

Water (purified/distilled): **1 L**

Clearing
20–60 minutes

Plain water

Toning
20–60 minutes

Potassium hexacyanoferrate(II)
(Potassium ferrocyanide)
100–120 g

Water (purified/distilled): **1 L**

Washing
30–60 minutes

Plain water

Cuprotype, Patterson process (2007)

Sensitizer

Copper(II) sulfate
pentahydrate
12 g

Iron(III) ammonium citrate
green
12 g

Water (purified/distilled): **100 mL**

Developing/fixing
3–5 minutes

Ammonium thiocyanate
10 g

Citric acid
5 g

Water (purified/distilled): **1 L**

Clearing
1–2 minutes

Citric acid
1 g

Water (purified/distilled): **1 L**

Toning
5–15 minutes

Potassium hexacyanoferrate(III)
(Potassium ferricyanide)
20 g

Water (purified/distilled): **1 L**

Washing
30–60 minutes

Plain water

> The photochemistry of the iron–citrate coordination compound is not yet well understood, and a detailed examination of this topic—still so uncertain even within the scientific community—lies beyond the scope of this text. It is therefore advisable, in this context, to adhere strictly to the facts that are generally accepted. The aim of this brief appendix is to provide the essential information needed to outline the basic principles underlying the photochemistry of iron and its coordinated organic compounds.[1]

Light and Photochemistry

Light is **radiant energy** consisting of electromagnetic waves, which can be emitted or absorbed in discrete, indivisible packets of energy—**photons**—or quanta of light.

Photochemistry studies and describes the chemical behavior of molecules whose electronic systems are **excited**[2] as a result of radiation absorption. It is based on the principle that a molecule in such an excited state represents a chemical species different from that corresponding to the ground, or non-excited, state.
If the lifetime of the excited state is sufficiently long, the distribution of electrons and the molecular geometry differ from those of the ground state, making it possible to observe distinct differences in chemical properties.[3]

Fundamental Laws

Photochemical theory began with the law formulated by **Grotthuss (1817)** and **Draper (1843)**, which states that only those radiations absorbed by a substance are photochemically active.

When a molecule absorbs a photon, its intrinsic energy increases and it is said to be in an excited state. This is a temporary condition: sooner or later, the excess energy will be transformed and dissipated, and the molecule will return to its ground energy state.

According to the law proposed by **Stark (1908–1912)**, **Einstein (1912–1913)**, and **Bodenstein (1913)**, the absorption of light by a molecule—which constitutes the so-called **primary photochemical process**—is a *one-quantum* process.[4]

The Photochemistry of Iron

Specifically, the mechanism responsible for the chemical reduction of copper during the exposure of a cuprotype sensitizer has never been thoroughly investigated. However, the corresponding mechanism in **cyanotype**—based on the same fundamental principles and on the photochemical behavior of iron compounds—has been studied in greater detail. It is therefore a good starting point to refer to what occurs in cyanotype, a better-known and more extensively explored technique, even though its mechanisms have not yet been completely clarified.
It is generally accepted that the light-induced reaction leading to the reduction of **iron(III)** to **iron(II)** constitutes the **primary photochemical process**: the resulting **iron(II)** then reacts with **ferricyanide** to form the well-known **Prussian/Turnbull's blue**. In **cuprotype**, by contrast, the **iron(II)** reacts with **copper**(II), reducing it to **copper**(I).

Cyanotype :

$$\mathit{UV} + \mathrm{Fe}^{3+} \longrightarrow \mathrm{Fe}^{2+} + \text{ferricyanide ion} = \text{blue pigment}$$

Cuprotype :

$$\mathit{UV} + \mathrm{Fe}^{3+} \longrightarrow \mathrm{Fe}^{2+} + \mathrm{Cu}^{2+} = \mathrm{Cu}^{+} \xrightarrow{\textit{Chemical treatment}} \text{red pigment}$$

For the photochemically produced **iron(II)** to be incorporated into the pigment lattice,[5] it must first break its coordination bond with the **citrate ions. Iron(III)–citrate complexes** photolyze, under irradiation with wavelengths between **254 and 450 nanometers**[6] (ultraviolet and blue light), into **iron(II)** compounds and **carbon dioxide**.

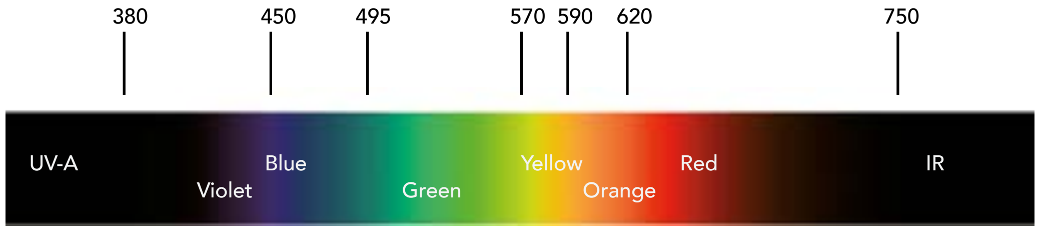


Fig. A2.1 — Electromagnetic spectrum ranging from the near ultraviolet (UV-A) to the near infrared (IR)

The energy of the radiation enables the **transfer of electrons** from the citrate to the metal: **iron(III)** are reduced to **iron(II)**, while the **citrate** is subsequently oxidized through **thermal decarboxylation**.[7]

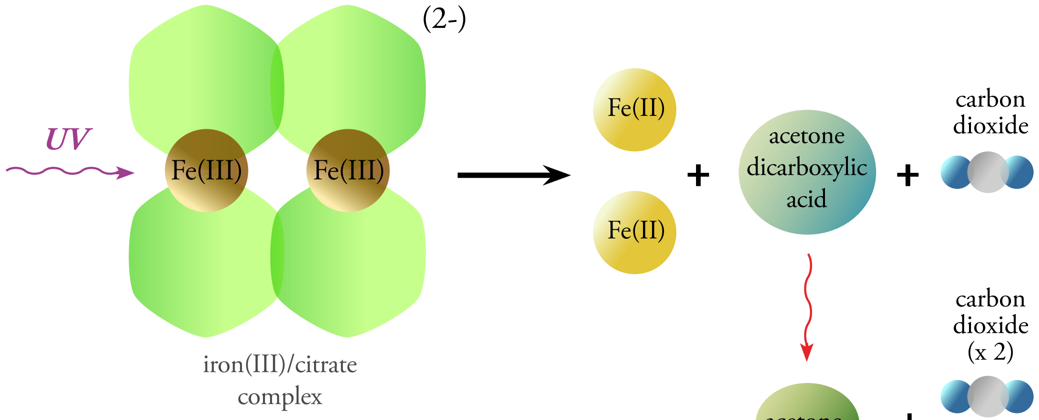


Fig. A2.4 — The structures of the iron(III)/citrate complex vary; the one shown is only one of them.

The Chloride Radical

A higher **photochemical efficiency** has been observed in **cuprotype sensitizers** containing the **chloride ion** (mainly in the *Carminio* and *Hematotype* processes). This can be explained by assuming that, in the **primary photochemical process**, this ion contributes to the formation of **radical species** (A'· in Fig. A2.3).

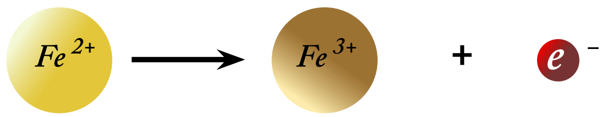
In fact, as already mentioned, the Fe^{3+} ion and its labile compounds with chloride ions undergo, under ultraviolet irradiation, a photoreduction that produces the Fe^{2+} ion and a chloride radical (Cl·).[16]
This radical can reduce an unexcited complex, leading to the formation of the final products (Fe^{2+}) with a **quantum yield** higher than that obtained with **ferric ammonium citrate** alone.

Copper Redox Reaction

The **divalent iron, Fe(II)**, generated as an initial product of the photoreduction of the sensitized layer, plays a crucial role in initiating the **redox reactions**[17] that lead to the **chemical reduction of copper**.

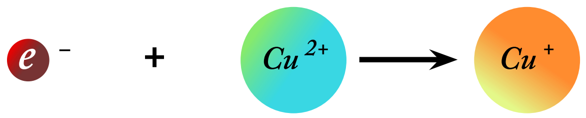
In this oxidation state, iron is unstable, especially in an **acidic environment** (such as that present in the sensitized layer), and tends to **donate an electron**, becoming oxidized to its more stable **trivalent form, Fe(III)**:

Fig. A2.5



The Electrons donated by **Fe(II)** ions are transferred to the copper species, which are thereby reduced:

Fig. A2.6



Once the series of reactions leading to the reduction of copper has been initiated during the exposure phase, light has completed its role.
The subsequent chemical treatments will then transform the layer of reduced copper into a stable cuprotype image.

Notes

1. Coordination compounds, also called complexes, are chemical substances in which a metal atom or ion coordinates, that is, directly binds to a certain number of neutral molecules or negative ions, called ligands. In the case of ferric ammonium citrate, the iron binds to citric acid (the ammonia is not directly bonded to it). *(Author's note)*
2. The excited state is the condition of an atom when one of its electrons occupies an energy level higher than that of its normal, or ground, state. *(Author's note)*
3. *Enciclopedia internazionale di chimica. [5: Fos-In]* (1972), Roma, Novara, Pem, p.103
4. *Enciclopedia internazionale di chimica. [5: Fos-In]* (1972), Roma, Novara, Pem, p.104

Author's note

Before addressing the topic of chemical risk, it must be noted that in the specific case of cuprotype there is no substance that can be defined as intrinsically hazardous. The precautions to be taken are the same as those that should be observed when handling other chemical substances encountered in everyday life. In addition to this, it should be emphasized that:

- The quantities of reagents required for the practices described in this text are rather small.
- The pictograms on the labels of the reagents indicate the hazards associated with the pure, concentrated product.
- The practices described in this text involve the use of highly diluted solutions of the mentioned reagents; this results in a significantly lower risk, both for the practitioner and for the environment.
- The fundamental starting point is to be aware of one's actions and to know that one is handling potentially hazardous substances—the same principle applies both to artists' materials and to household detergents.
- By adopting clean and rational working methods, combined with the use of minimal personal protective equipment (PPE), the risk is further reduced.[1]

Risks Related to the Use of Chemical Substances

The use of any chemical substance—whether natural or industrially produced—always entails the acceptance of a **generic risk** by the user. Even an apparently harmless operation, such as **squeezing a lemon**, carries a generic risk.

The handling of a chemical reagent does not, in itself, necessarily entail an **actual health risk**, as this depends solely on the **toxicological characteristics** of the substance and, accordingly, on the **mode of contact** that may occur during practical activity.
For this reason, **chemical risk** is related to the **type of substance**, its **quantity**, and the **duration of exposure**, taking into account the possible **routes of entry** into the human body.[2]

Chemical agents can penetrate the human body and may cause **anatomical or functional damage**, whether **generalized or localized**, **temporary or permanent**, **immediate or delayed** over time.
Even a **direct action** on the **skin barrier** or **mucous membranes** can be considered a form of penetration into the body, since any harmful effect manifests itself in the cells that constitute these barriers.
The **harmful action** of a substance depends not only on its chemical-physical **characteristics**, but also on its **route of entry** into the body, its **ability to diffuse and localize** in various organs, possible **inactivation mechanisms**, and **routes of elimination**. The main **routes of entry** into the body are:

1. Inhalation
2. Cutaneous (through the skin)
3. Ingestion

1. Absorption by Inhalation

This is the most frequent route of absorption and occurs when the chemical substance is present in the form of gas, fumes, vapors, or aerosols.
The effect may be limited to the upper respiratory tract (irritative phenomena) or may damage the lungs.
Irritative, acute, or chronic effects may occur, characterized by inflammation, congestion, and edema. As a consequence of repeated acute inflammatory episodes, chronic bronchopulmonary disorders such as bronchitis and bronchiolitis, peribronchial and perivascular fibrosis, pulmonary fibrosis, and emphysema may develop.

2. Absorption Through the Skin

The skin normally serves as a barrier between the body and the external environment; however, an increasing number of substances have been found to present a significant risk of cutaneous absorption, not only through direct contact, but also through exposure of the skin to vapors of the substance itself.

Penetration occurs more easily whenever the integrity of the skin is compromised. Direct contact with, or exposure of the skin to, irritant chemical vapors can cause inflammatory reactions of varying severity.

Some substances have a photosensitizing effect, making the skin hypersensitive to subsequent exposure to sunlight. Finally, since the skin is responsible for eliminating waste products, it may occur that internal intoxications lead to cutaneous disorders, resulting from the body's attempt to expel toxic substances through this route.

3. Absorption by Ingestion

Accidental ingestion may occur:
- by **mouth pipetting** of solutions;
- due to **splashes or sprays** entering the mouth as a result of accidents;
- due to **chemical products being transferred to the mouth by hand contact**.

Symptoms related to the ingestion of chemical substances may include **nausea, vomiting, abdominal pain**, and, in more severe cases, **profuse diarrhea**, acute abdomen **due to perforation**, and **ulcers**.[3]

Basic Rules for the Use and Handling of Chemical Substances

- **Consult the safety data sheets (SDS)** to assess the chemical–physical characteristics of the substance and establish the most appropriate procedures for its safe use in the laboratory.
- **Identify the potential routes of entry** of the substances used and determine the appropriate **personal protective equipment (PPE)** to be worn in order to prevent possible health issues for the practitioner.
- **Never pipette liquids by mouth**; always use **plunger pipettes, dispensers**, or similar devices.
- **Avoid any contact** of chemical substances with the skin; in case of accidental contact, **rinse immediately with plenty of water**.
- Always use **hazardous substances***, if possible, **under a fume hood** or in a **well-ventilated area**, while wearing the proper PPE.

* The only chemical substance mentioned in this text that is recognized as **acutely toxic** is **potassium dichromate** (and **ammonium dichromate**), both of which are classified as **carcinogenic to humans**.
However, their use in **cuprotype** is **strictly optional**. Any use that may occur is intended **in aqueous solution** and in very **small quantities**.

List of Chemical Substances and Related Hazards [4]

When handling any chemical substance, it should be considered standard practice to always wear the **minimum laboratory protective equipment**—that is, **safety goggles**, a **lab coat or apron**, and **latex gloves**—along with any additional precautions as necessary.
During the use of any chemical substance, one must operate under conditions of total safety, in order to prevent contact of the substance with **eyes, skin**, or **clothing**. After handling, **hands must be thoroughly washed**.

When a chemical substance is **not in use**, it must be **stored in a tightly closed, properly labeled container**, in an appropriate place **inaccessible to children**.

The information that follows has been **condensed from the safety data sheets** of the substances involved in preparing the **chemical solutions necessary for cuprotype**. The **hazard classifications** are summarized according to **EU Regulation (EC)** using **CLP pictograms** and symbols that describe the type of risk.

Physical and chemical hazards


Explosive


Gas under pressure


Flammable


Oxidizing


Corrosive

Health hazards


Acute toxicity


Serious health effects


Less severe health effects

Environmental hazards


Hazardous to the environmen

Ammonium bromide
CAS No. 12124-97-9

Regulation (EC) n. 1272/2008
CLP pictogram:

Warning: Danger

Hazard statements

H319	Causes serious eye irritation
H336	May cause drowsiness or dizziness
H360FD	May damage fertility; May damage the unborn child
H362	May cause harm to breast-fed children
H372	Causes damage to organs through prolonged or repeated exposure

Precautionary statements
P260 Do not breathe dust/fume/gas/mist/vapors/spray
P280 Wear protective gloves/protective clothing/eye protection/face protection

Ammonium dichromate
CAS No. 7789-09-5

Regulation (EC) n. 1272/2008
CLP pictogram:

Warning: Danger

Hazard statements

H272	May intensify fire; oxidiser
H301	Toxic if swallowed
H312	Harmful in contact with skin
H314	Causes severe skin burns and eye damage
H317	May cause an allergic skin reaction
H330	Fatal if inhaled
H334	May cause allergy or asthma symptoms or breathing difficulties if inhaled
H340	May cause genetic defects
H350	May cause cancer
H360FD	May damage fertility; May damage the unborn child
H372	Causes damage to organs through prolonged or repeated exposure
H400	Very toxic to aquatic life
H410	Very toxic to aquatic life with long lasting effects

Precautionary statements

P201	Obtain special instructions before use
P220	Keep/Store away from clothing and other combustible materials
P260	Do not breathe dust/fume/gas/mist/vapors/spray
P273	Avoid release to the environment
P280	Wear protective gloves/protective clothing/eye protection/face protection

Ammonium hydroxide; Ammonia (10% solution)
CAS No. 1336-21-6

Regulation (EC) n. 1272/2008
CLP pictogram:

Warning: Danger

Hazard statements

H290	May be corrosive to metals
H314	Causes severe skin burns and eye damage
H335	May cause respiratory irritation
H410	Very toxic to aquatic life with long lasting effects

Precautionary statements

P273	Avoid release to the environment
P280	Wear protective gloves/protective clothing/eye protection/face protection

Ammonium thiocyanate
CAS No. 1762-95-4

Regulation (EC) n. 1272/2008
CLP pictogram:

Warning: Caution

Hazard statements
H302 Harmful if swallowed
H312 Harmful in contact with skin
H332 Harmful if inhaled
H412 Harmful to aquatic life with long lasting effects

Precautionary statements
P261 Avoid breathing dust/fume/gas/mist/vapours/spray
P273 Avoid release to the environment
P280 Wear protective gloves/protective clothing/eye protection/face protection

Citric acid (Monohydrate)
CAS No. 5949-29-1

Regulation (EC) n. 1272/2008
CLP pictogram:

Warning: Caution

Hazard statements
H319 Causes serious eye irritation
H335 May cause respiratory irritation

Precautionary statements
P261 Avoid breathing dust/fume/gas/mist/vapours/spray
P280 Wear protective gloves/protective clothing/eye protection/face protection

Copper(II) chloride (Dihydrate)
CAS No. 10125-13-0

Regulation (EC) n. 1272/2008
CLP pictogram:

Warning: Danger

Hazard statements
H290 May be corrosive to metals
H302+H312 Harmful if swallowed or in contact with skin
H315 Causes skin irritation
H318 Causes serious eye damage
H410 Very toxic to aquatic life with long lasting effects

Precautionary statements
P273 Avoid release to the environment
P280 Wear protective gloves/protective clothing/eye protection/face protection

Copper(II) sulfate (Pentahydrate)
CAS No. 7758-99-8

Regulation (EC) n. 1272/2008
CLP pictogram:

Warning: Danger

Hazard statements
H302 Harmful if swallowed
H318 Causes serious eye damage
H410 Very toxic to aquatic life with long lasting effects

Precautionary statements
P273 Avoid release to the environment
P280 Wear protective gloves/protective clothing/eye protection/face protection

EDTA; disodium salt Dihydrate (Ethylenediaminetetraacetic acid Dihydrate)

CAS No. 6381-92-6

Regulation (EC) n. 1272/2008
CLP pictogram:

Warning: Caution

Hazard statements
H332 Harmful if inhaled
H373 May cause damage to organs through prolonged or repeated exposure

Precautionary statements
P260 Do not breathe dust/fume/gas/mist/vapors/spray
P264 Wash hands thoroughly after handling
P270 Do not eat, drink or smoke when using this product
P280 Wear protective gloves/protective clothing/eye protection/face protection

Hydrochloric acid 37%

CAS No. 7647-01-0

Regulation (EC) n. 1272/2008
CLP pictogram:

Warning: Danger

Hazard statements
H290 May be corrosive to metals
H314 Causes severe skin burns and eye damage
H335 May cause respiratory irritation

Precautionary statements
P261 Avoid breathing dust/fume/gas/mist/vapours/spray
P280 Wear protective gloves/protective clothing/eye protection/face protection

Hydrogen peroxide (3% solution)

CAS No. 7722-84-1

egulation (EC) n. 1272/2008
CLP pictogram:

Warning: Caution

Hazard statements
H319 Causes serious eye irritation

Precautionary statements
P280 Wear protective gloves/protective clothing/eye protection/face protection

Iron(II) ammonium sulfate (Hexahydrate)

CAS No. 7783-85-9

Regulation (EC) n. 1272/2008
CLP pictogram: Not required

Warning: Substance or mixture not classified as hazardous according to regulation

Hazard statements
No hazard statement (s)

Precautionary statements
No precautionary statement(s) required

Iron(II) sulfate (Heptahydrate)
CAS No. 7782-63-0

Regulation (EC) n. 1272/2008
CLP pictogram:

Warning: Danger

Hazard statements
H302 Harmful if swallowed
H315 Causes skin irritation
H319 Causes serious eye irritation

Precautionary statements
P280 Wear protective gloves/protective clothing/eye protection/face protection

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Iron(III) ammonium citrate (green type: Fe 12.5-14%)
CAS No. 1185-57-5

Regulation (EC) n. 1272/2008
CLP pictogram: Not required

Warning: Substance or mixture not classified
as hazardous according to regulation

Hazard statements
No hazard statement (s)

Precautionary statements
No precautionary statement(s) required

Iron(III) chloride (Anhydrous)
CAS No. 7705-08-0

Regulation (EC) n. 1272/2008
CLP pictogram:

Warning: Danger

Hazard statements
H290 May be corrosive to metals
H302 Harmful if swallowed or in contact with skin
H315 Causes skin irritation
H317 May cause an allergic skin reaction
H318 Causes serious eye damage

Precautionary statements
P280 Wear protective gloves/protective clothing/eye protection/face protection

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Potassium dichromate
CAS No. 7778-50-9

Regulation (EC) n. 1272/2008
CLP pictogram:

Warning: Danger

Hazard statements
H272 May intensify fire; oxidiser
H301 Toxic if swallowed
H312 Harmful in contact with skin
H314 Causes severe skin burns and eye damage
H317 May cause an allergic skin reaction

H330	Fatal if inhalated
H334	May cause allergy or asthma symptoms or breathing difficulties if inhaled
H340	May cause genetic defects
H350	May cause cancer
H360FD	May damage fertility; May damage the unborn child
H372	Causes damage to organs through prolonged or repeated exposure
H410	Very toxic to aquatic life with long lasting effects

Precautionary statements

P201	Obtain special instructions before use
P220	Keep/Store away from clothing and other combustible materials
P260	Do not breathe dust/fume/gas/mist/vapors/spray
P273	Avoid release to the environment
P280	Wear protective gloves/protective clothing/eye protection/face protection
P284	Wear respiratory protection

Potassium hexacyanoferrate(II) Hydrated; Potassium ferrocyanide (Trihydrate)

CAS No. 14459-95-1

Regulation (EC) n. 1272/2008
CLP pictogram: Not required

Warning: Substance or mixture not classified as hazardous according to regulation

Hazard statements

No hazard statement (s)

Precautionary statements

No precautionary statement(s) required

Potassium hexacyanoferrate(III); Potassium ferricyanide

CAS No. 13746-66-2

Regulation (EC) n. 1272/2008
CLP pictogram:

Warning: Caution

Hazard statements

H319	Causes serious eye irritation
H411	Toxic to aquatic life with long lasting effects
EUH032	Contact with acids liberates very toxic gas

Precautionary statements

P264	Wash hands thoroughly after handling
P273	Avoid release to the environment
P280	Wear protective gloves/protective clothing/eye protection/face protection

Potassium thiocyanate

CAS No. 333-20-0

Regulation (EC) n. 1272/2008
CLP pictogram:

Warning: Danger

Hazard statements

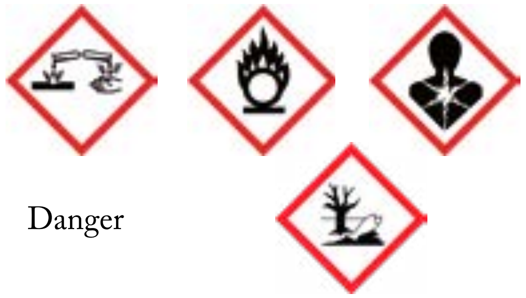
H302	Harmful if swallowed or in contact with skin
H312+ H332	Harmful in contact with skin or if inhaled
H318	Causes serious eye damage
H412	Harmful to aquatic life with long lasting effects

Precautionary statements

P273	Avoid release to the environment
P280	Wear protective gloves/protective clothing/eye protection/face protection

Silver nitrate
CAS No. 7761-88-8

Regulation (EC) n. 1272/2008
CLP pictogram:



Warning: Danger

Hazard statements

H272	May intensify fire; oxidizer
H290	May be corrosive to metals
H314	Causes severe skin burns and eye damage
H360D	May damage the unborn child
H410	Very toxic to aquatic life with long lasting effects

Precautionary statements

P220	Keep/Store away from clothing and other combustible materials
P273	Avoid release to the environment
P280	Wear protective gloves/protective clothing/eye protection/face protection

Sodium citrate tribasic (Dihydrated)
CAS No. 6132-04-3

Regulation (EC) n. 1272/2008
CLP pictogram: Not required

Warning: Substance or mixture not classified as hazardous according to regulation

Hazard statements

No hazard statement (s)

Precautionary statements

No precautionary statement(s) required

Sulfuric acid 96%
CAS No. 7664-93-9

Regulation (EC) n. 1272/2008
CLP pictogram:

Warning: Danger

Hazard statements

H290	May be corrosive to metals
H314	Causes severe skin burns and eye damage

Precautionary statements

P234	Keep only in original container/packaging
P280	Wear protective gloves/protective clothing/eye protection/face protection

Tween 20® (Polisorbate 20)
CAS No. 1336-21-6

Regulation (EC) n. 1272/2008
CLP pictogram: Not required

Warning: Substance or mixture not classified as hazardous according to regulation

Hazard statements

No hazard statement (s)

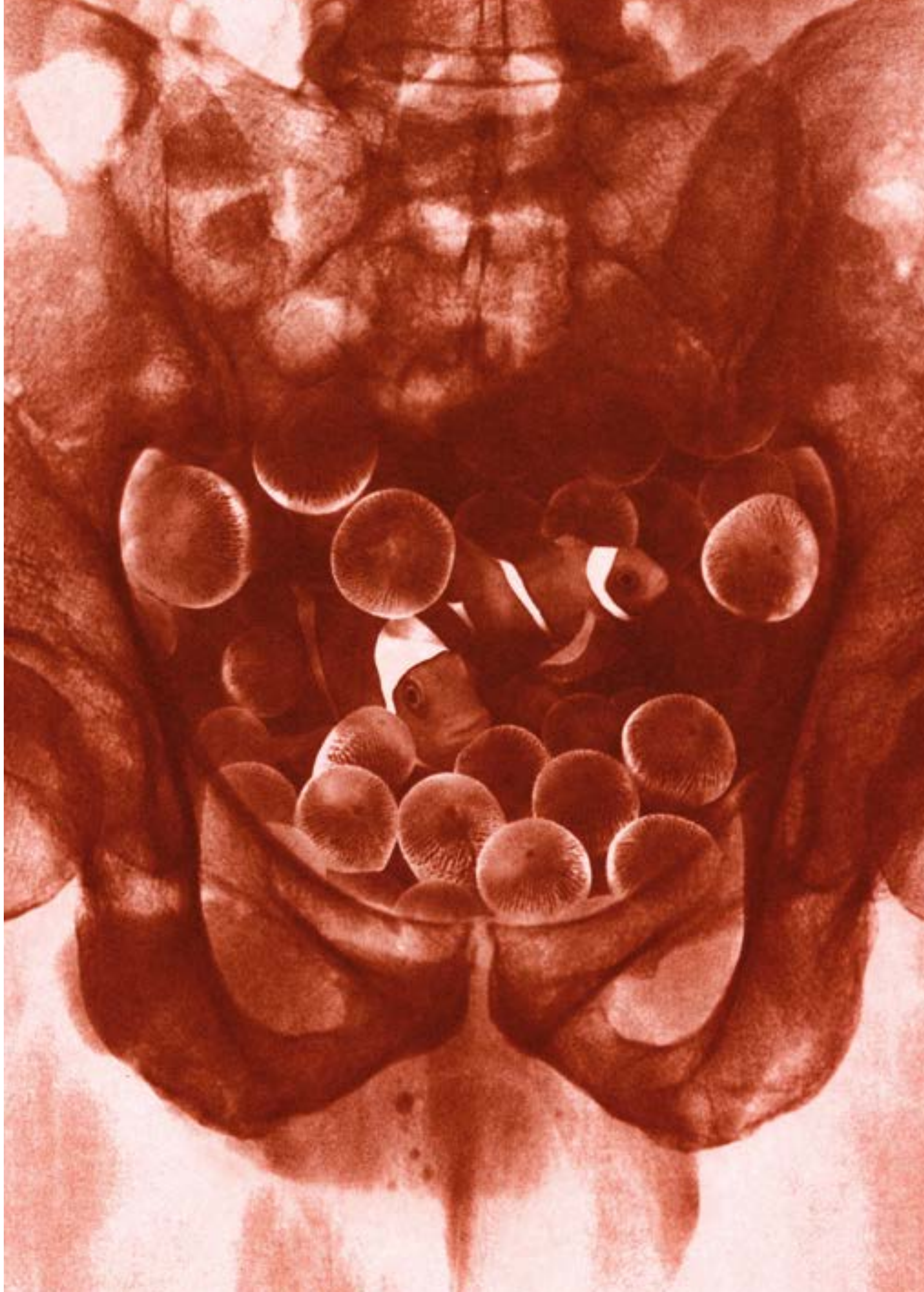
Precautionary statements

No precautionary statement(s) required

Notes

1. Ware Mike (2016), *Cyanomicon (II). History, Science and Art of Cyanotype: photographic printing in Prussian blue,* p. 174 <https://www.mikeware.co.uk/downloads/Cyanomicon_II.pdf>
2. Università degli studi di Palermo, *Il rischio chimico*, p. 147 <https://www.unipa.it/dipartimenti/difc/.content/documenti/Sicurezza_files/rischio_chimico.pdf>
3. Università degli studi di Palermo, *Il rischio chimico*, pp. 152,153 <https://www.unipa.it/dipartimenti/difc/.content/documenti/Sicurezza_files/rischio_chimico.pdf>
4. Not all of the chemical substances mentioned in the book are included in this list — only those expected to be used, including optional ones. *(Author's note)*

Next page (233): *Inner Condition (Motherhood)*
Printed in cuprotype, Carmine process, on Fabriano Unica paper (250 g/m^2)



Acknowledgments

Even after one hundred and seventy years since the invention of the first photographic printing process based on copper salts, the traces left by the pioneers of photography have been preserved in historical documents.
The invention, development, and modernization of Cuprotype are the result of the efforts of a small number of innovative experimenters.
It may be superfluous to state—but I would be remiss not to—that, in order to complete this book, I have incurred a debt of gratitude toward them. I therefore wish to begin this page by expressing my admiration for the work of C.J. Burnett, J.B. Obernetter, Jim Patterson, and Mike Ware, from whose studies I have drawn numerous theoretical and experimental insights, some of them decisive.

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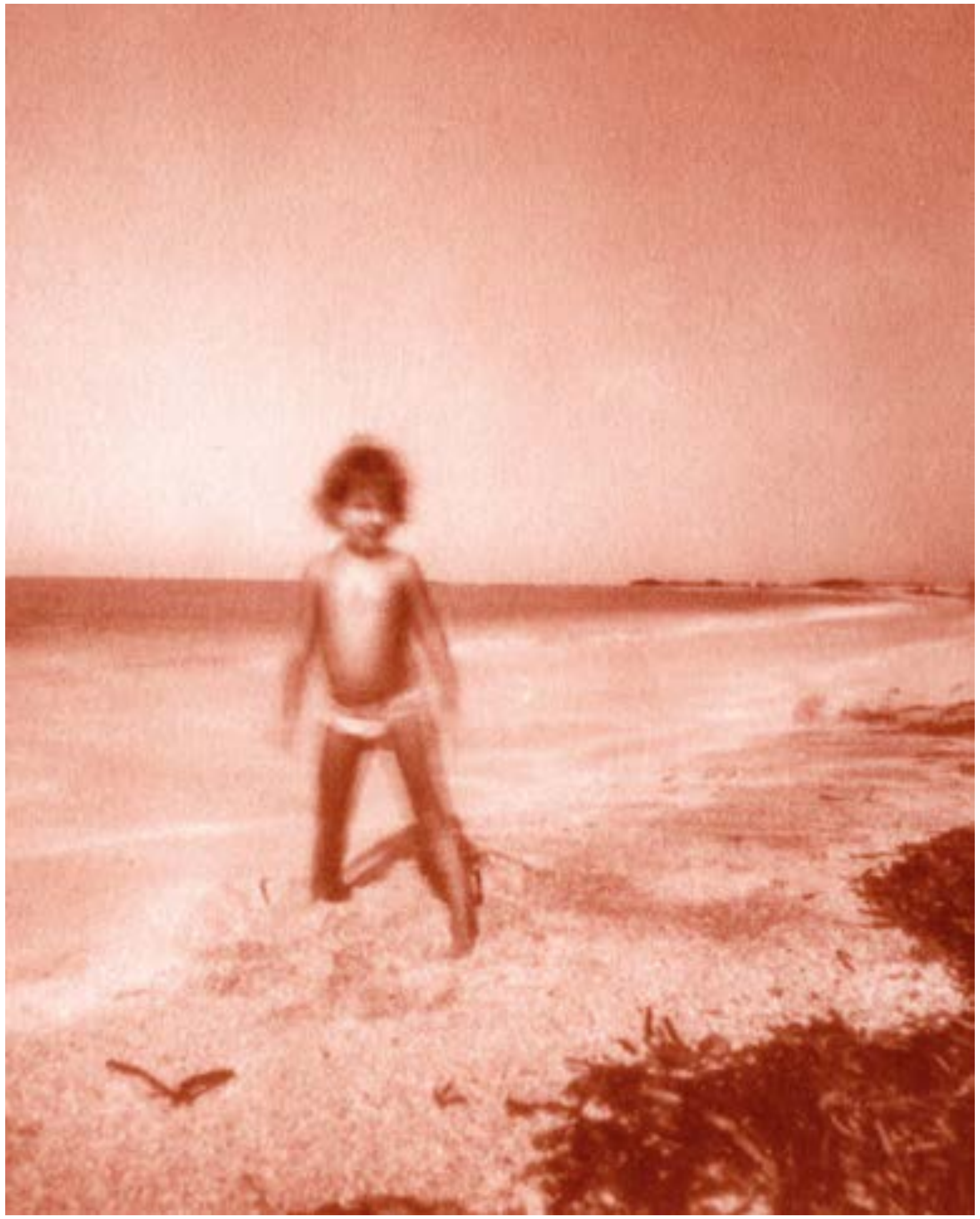
A special word of thanks goes to two women, the same ones who stand beside me every day, and to whom I owe a debt far greater than words can express. This book might never have been written without the love and support of Elena and Emma, for having listened to and read, with something that almost resembled interest, my endless explanations about the differences between ferrocyanides and ferricyanides, and my theories on the influence of pH in pigment formation.
Both deserve further gratitude: Elena, for reading, checking, smoothing the rough edges, and polishing the imperfections of every page of the original Italian version of the book as it was being written; and Emma, for her keen eye for typos and her remarkable motivational skills.

Last, but certainly not least, I would like to gratefully thank my parents-in-law, Anna and Giovanni, for having generously offered me shelter (they know).



Emma
(Pinhole photograph)
Print in cuprotype, Carminio process, on Hahnemühle Platinum Rag paper (300 g/m^2).

This volume is an English translation of *La via del rame: Cuprotipia, ricerca su un antico processo di stampa fotografica* (2025). Minor differences from the original Italian edition may be found, introduced in the course of the translation.

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