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Preface

Meeting Maestro Caniparoli is a singular experience—both for his personality and for the depth of his knowledge of practices and techniques that reemerge from the mists of time in renewed splendor.
The Copper Way offers the reader a historical, technical, and scientific account of the historic photographic technique of cuprotype, which can be placed among the early nineteenth-century researches aimed at reproducing reality through those processes that we now call "photography."

Through the historical figures of the pioneers Charles John Burnett and Johann Baptist Obernetter, and up to Jim Patterson's process with its modern reinterpretation, Caniparoli invites us to view cuprotype as a field of research into photosensitive substances—one that continues to attract the interest of artists and practitioners of historic processes.

The historical ambiguities and uncertainties of an experimental technique, which call into question the chemistry of the reddish-brown pigment (typical of copper tones), have not discouraged the author from treating the process as "a continuous exploration"—a path capable of pushing the artist toward a critical vision.

In keeping with a contemporary and necessary sensitivity, the book includes a section dedicated to safety and environmental considerations, providing detailed guidelines for minimizing risks during the various stages of development and production, including the use of protective equipment in the laboratory. The cuprotype, however, shows a much lower toxicity than other photographic or printmaking techniques.

The volume The Copper Way thus stands not only as a technical manual but, above all, as an artist's meditation on cuprotype and on photography in general. Balancing thought and practice, Caniparoli invites the reader to approach this printing process as an unexplored terrain—guiding them through reflection while maintaining a constant stylistic tension between scientific rigor and free interpretation.

Finally, by emphasizing the importance of personal research and passion cultivated beyond academic frameworks, this preface wishes to serve as an encouragement for the creation of new artistic research paths that place experimentation at the center of learning.
It urges professors in Fine Arts Academies to promote not only the teaching of techniques, but also the rigor and curiosity that animate every authentic creative activity—remaining faithful to the laboratory spirit that these institutions should preserve and nurture as spaces devoted to reflection and the unforeseen.
It was, in fact, at the Academy of Fine Arts in Bari that I invited Vincenzo Caniparoli to lead a workshop on this alternative printing technique in the spring of 2023—later deepened in 2024—with the result of great interest among students in photosensitive languages and technologies applied to printmaking, of which he is a true master.

Grazia Tagliente

Professor of Printmaking Techniques
Head of Internationalization
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Member of the National Council for Higher Education in the Arts (CNAM)
Section II – Visual Arts

Bari, November 2024

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-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 "contaminate" the original processes of both Obernetter and Burnett, a distortion that has been transmitted up to our own day.

Ancient 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

To my family
— present and past.

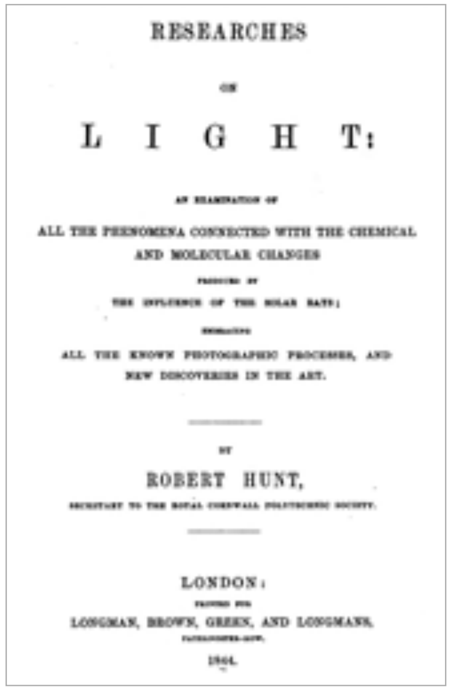
I

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]

Similar articles appeared in other periodicals, such as the *Photographic Journal* (Liverpool and Manchester),[7] in 1857, confirming that year as the moment when the process was first made public. Burnett's **cuprotype** thus preceded by several years the **iron-cupric process** of **Obernetter** (1864).

> It should be clarified that, when referring to the cuprotype, in connection with Burnett's copper-based process, the term denotes the **copper chromate process**, which originated as a modification of Hunt's **chromatype**.
> The **uranium–copper** process, also attributed to Burnett—and sometimes incorrectly identified as the cuprotype—was introduced later.

Like Hunt before him, Burnett was a passionate experimenter of the **photochemical properties of metallic salts**, and he was the first to produce photographic prints using **uranium salts** as sensitizers.
He described the **uranotype process** at the 1855 meeting of the *British Association for the Advancement of Science in Glasgow.*[8]

According to the *Encyclopedia of Nineteenth-Century Photography* (2008),[9] Charles John Burnett is credited with the following processes:

- **Uranotype** (1855)
- **Palladiotype** (1856)
- **Cuprotype** (1857)
- and, together with **Niépce de Saint Victor**, the **uranium print** (1857).

In **1891**, photographer **P.C. Duchochois** published *Photographic Reproduction Processes*, a treatise on non-silver printing methods.
In it appeared a recipe for a sensitizer made of **uranyl nitrate** and **copper nitrate**, attributed to Burnett under the name **cuprotype**.
Duchochois based his description on Burnett's original articles from *Photographic Notes* (vol. II, 1857), which he reproduced in full.[10]

However, none of Burnett's writings cited by Duchochois contains any **direct reference** to a sensitizer based on copper and uranium nitrates.

The uranium-based formula also appeared in the Bullettino della Società Fotografica Italiana (1891), in an article titled **"Procedimento di cuprotipia del signor Barnett"**, which reads as follows:

> «The new process, which we now undertake to describe, serves to obtain positives on paper using the ordinary printing frames, and takes its name from one of the metals forming the sensitive solution; however, we believe that this process would be more appropriately named cuprouranotype, since, in our opinion, it is more specifically to the sensitivity of the uranium salt than to that of copper that the formation of the image by light is due».[11]


BULLETTINO
SOCIETÀ FOTOGRAFICA
ITALIANA
FIRENZE

Fig. 1.4 — *Bullettino della Società Fotografica Italiana*, fascicles 1–2, 1891.

What was written in the Bullettino was in fact taken from an article in *The Photographic Times*[12] (New York), whose ultimate source once again proved to be **Duchochois's book**.

From the continuous process of modification and innovation that characterizes Burnett's work, it is reasonable to infer that experiments along these lines may indeed have been undertaken. However, no direct documentation of such trials has been found. In his writings published in the principal photographic journals of the time, Burnett explicitly stated that the idea of combining **copper and uranium** in the cuprotype dated from **1857**, motivated by the desire to obtain **more neutral tones** than those achieved with iron toning, which he had previously adopted.

> In *Anthony's Photographic Bulletin* (1889), **Duchochois** correctly cites and attributes to Burnett the **original cuprotype formula**,[13] that is, the **copper chromate process**. Why, two years later (1891), he replaced it—without even mentioning the earlier version—with the **copper–uranium formula** remains unknown. There exists a gap of over thirty years between Burnett's original publications and the uranium formula attributed to him by Duchochois in 1891, and no evidence has been found to trace its origin or the time when it may have been devised. As things stand, the **only supporting evidence** for its attribution rests solely on **Duchochois's own words**.

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.

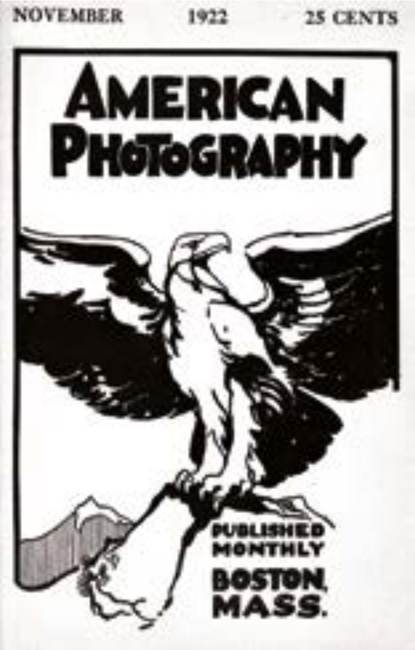


Fig. 1.6 — *American Photography*, cover, November 1922. Inside, Obernetter's process is mentioned in only four lines.

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]

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.

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:

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

Table 2.1

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.

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

Table 2.2

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).

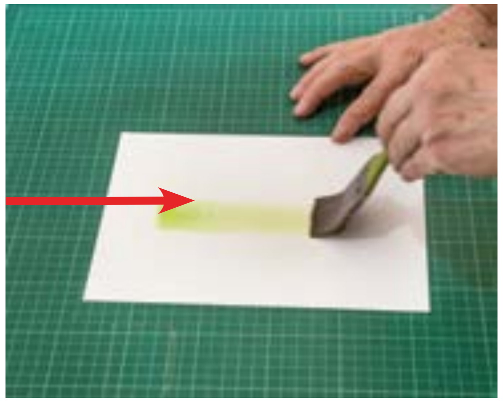


Fig. 2.16 — The sensitizer is first brushed parallel to the long side of the sheet.

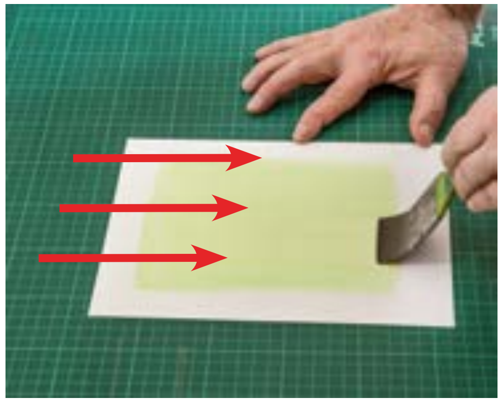


Fig. 2.17 — Continue brushing in the same direction until the entire desired area is evenly covered.

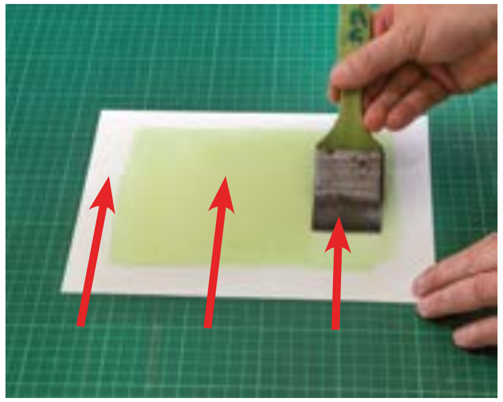


Fig. 2.18 — After coating the sheet uniformly along its long axis, the direction of the brushstrokes can be crossed. Continue brushing in both directions until no liquid pools remain on the paper surface.

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.

Chemical Reactions and Redox Processes

Before proceeding, it is essential to clarify two fundamental concepts: that of a **chemical reaction** and that of **oxidation–reduction** (**redox**).

A **chemical reaction** is a dynamic process that leads to the transformation of one or more substances. In classical chemistry, these reactions involve only the **negatively charged particles** of the atom—**the electrons**.

Chemical bonds are determined by the number and arrangement of electrons in the **outermost shells** of atoms. A chemical reaction is both the cause and the result of a **redistribution of electrons** within these outer energy levels. When it is stated that an atom (or molecule) has been **oxidized** or **reduced**, the reference is always to **electrons**—the negatively charged particles.

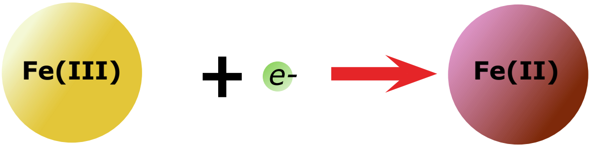


Fig. 2.20 — Trivalent iron, Fe(III), gains one electron (e–) and is reduced, becoming bivalent iron, Fe(II).

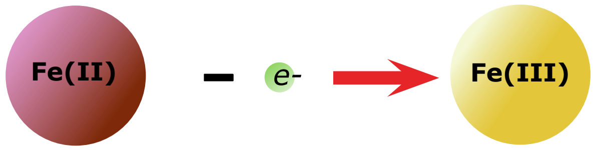


Fig. 2.21 — Bivalent iron, Fe(II), loses one electron (e–) and is oxidized, becoming trivalent iron, Fe(III).

- An atom is **oxidized** when it **loses electrons**, which makes it **more positive** (or less negative) from an electrostatic standpoint.
- An atom is **reduced** when it **gains electrons**, making it **more negative** (or less positive).

Oxidation and **reduction** are **natural tendencies** of atoms:

- **Metals** tend to **lose electrons**, and thus become **oxidized**.
- **Nonmetals**, on the other hand, tend to **gain electrons**, and therefore become **reduced**.

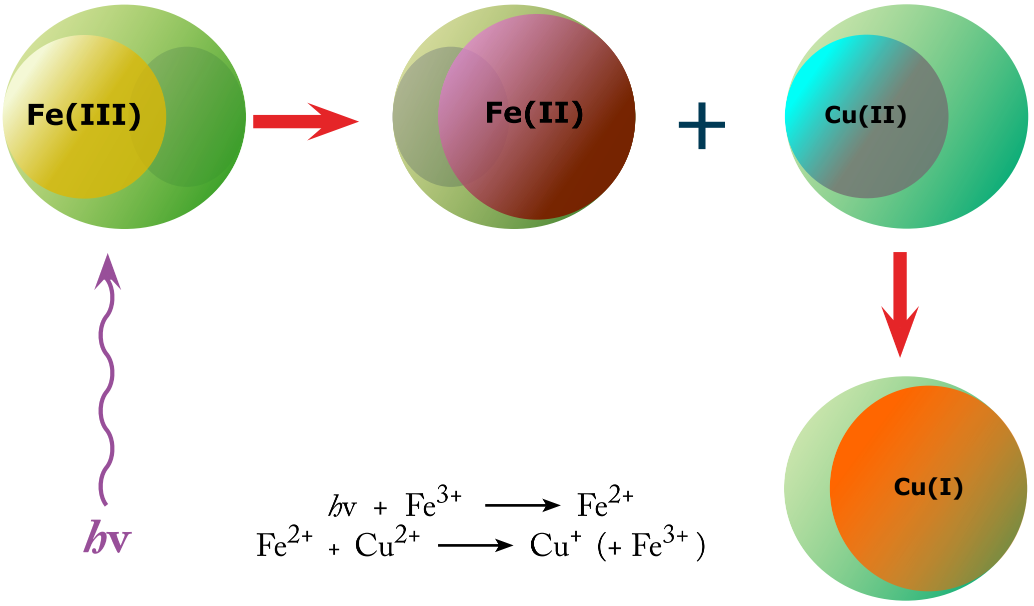
How it works: Photochemical Principles

> Within the scope of this text, to gain a basic understanding of the operations to be carried out, it is sufficient to know the **reactions** themselves, without worrying too much about **why** they occur.

During exposure, the sensitized sheet is irradiated with **ultraviolet light**. Each trivalent iron atom, Fe(III), that absorbs a photon of UV radiation (*hv*) is reduced to bivalent iron, Fe(II), through a photochemical process that will be schematically described in Appendix II.

The photoreduction of iron triggers a series of reactions that cause Fe(II) to promote the reduction of bivalent copper Cu(II) to monovalent copper Cu(I).[12]

In short:



$$h\nu + Fe^{3+} \longrightarrow Fe^{2+}$$
$$Fe^{2+} + Cu^{2+} \longrightarrow Cu^{+} \ (+ Fe^{3+})$$

Fig. 2.22 — Simplified diagram of the photochemical reaction induced by ultraviolet radiation (*hv*) on ferric ammonium citrate, with the subsequent chemical reduction of copper operated by the photoreduced iron.

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**.

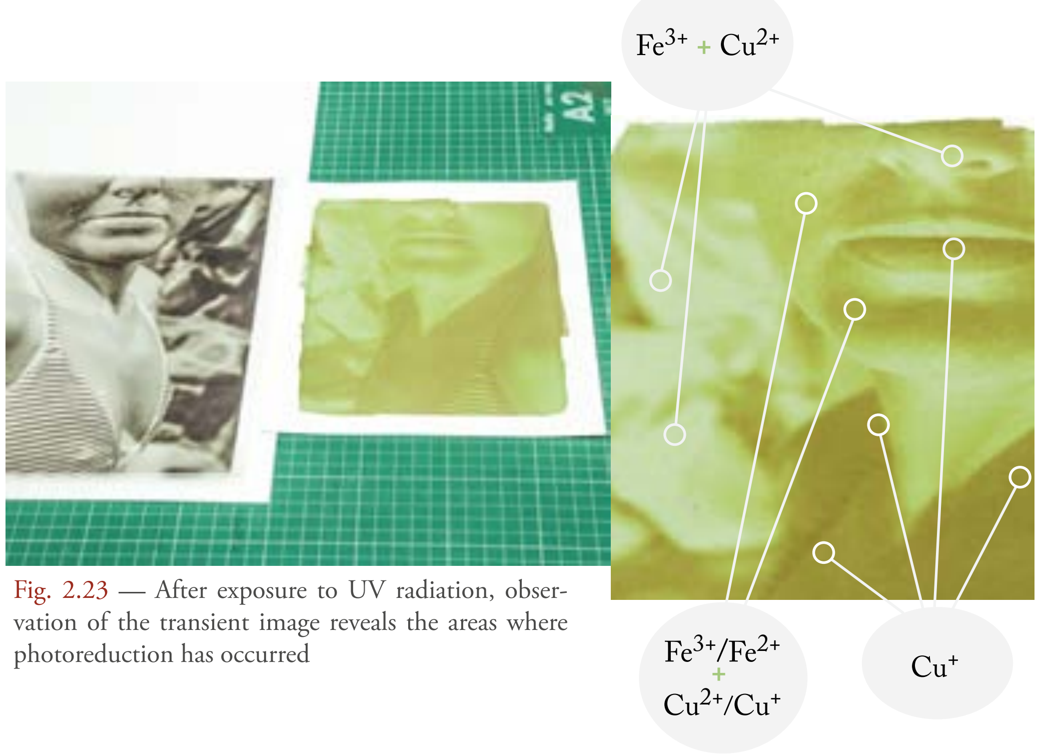


Fig. 2.23 — After exposure to UV radiation, observation of the transient image reveals the areas where photoreduction has occurred

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

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

where **Cu^{+}** is the monovalent copper cation and **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.

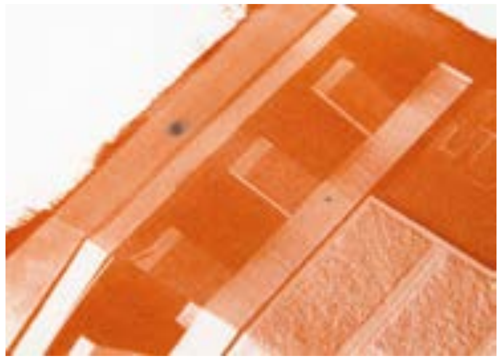


Fig. 2.30 — Bluish stains caused by insufficiently thorough washing.


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

From a chemical standpoint, this is an **oxidation-reduction (redox)** reaction, involving an electron transfer between **copper** and the **hexacyanoferrate(III)** complex. The solid cuprous thiocyanate is "consumed" by the potassium ferricyanide solution: the latter is reduced to **ferrocyanide**, while the copper is oxidized from **Cu(I)** to **Cu(II)**. A precipitate of **copper(II) dipotassium hexacyanoferrate(II)** is formed:[13]

$$\underset{\textit{Copper(I) thiocyanate}}{CuSCN_{(s)}} + \underset{\textit{Potassium hexacyanoferrate(III)}}{K_3[Fe(CN)_6]_{(aq)}} \longrightarrow \underset{\textit{Copper(II) potassium hexacyanoferrate(II)}}{CuK_2[Fe(CN)_6]_{(s)}\downarrow} + \underset{\textit{Potassium thiocyanate}}{KSCN_{(aq)}}$$

(s) = solid; (aq) =aqueous solution

The image is now, both in **appearance** and **chemical composition**, a true **cuprotype**. The pigment that composes it is similar in color to the one obtained by **Hatchett (1802)**, though **chemically distinct**.

Washing the Print

The print must be washed under **running water** to remove all residual **potassium ferricyanide**, a crucial step for obtaining a clean and stable image.

The duration of washing—**30 to 60 minutes**—depends on the type of paper used. Even slight yellowing will be clearly visible when the print is viewed in transmitted light and under backlighting.
Any yellowing of the fibers indicates the presence of residual ferricyanide, and the washing must therefore be extended.

During this phase, the **image contrast will gradually decrease**, and the **tone may shift** depending on the **pH and hardness** of the water.

Procedure

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

Table 2.13

Drying the Print

Before drying, ensure that the **washing was thorough**—the paper background should match the color of the original sheet. If the wash check is successful, proceed to **dry the print**.
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 **strong heat sources**—including **direct sunlight**—must be avoided.

Fig. 2.35 — The final color of the dry print varies depending on the type of paper used, while the resulting contrast and density are generally of medium level.

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

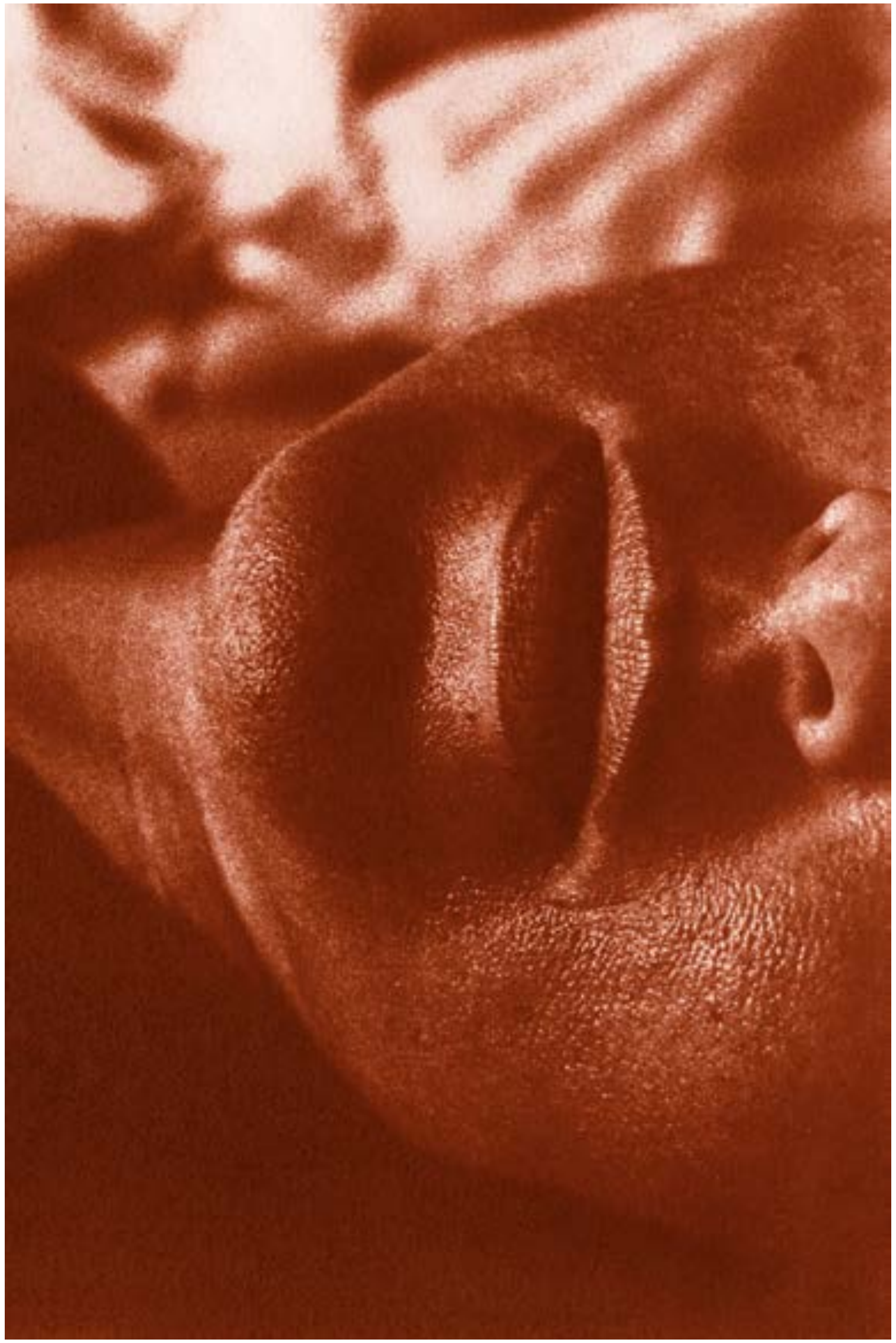
Notes:

- 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.



III

An Alternative Solution:
The Carminio Method

A Matter of Solubility

Patterson's sensitizer solution consists of **copper sulfate** and **iron(III) ammonium citrate**—a simple mixture.

Copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) is a blue crystalline compound, **moderately soluble in water** at room temperature, with a solubility of **316 g/L** (grams per liter). A saturated solution reaches about **31% w/v**.

Ferric ammonium citrate, on the other hand, is **much more soluble**, with a solubility of **1200 g/L** at room temperature—corresponding to about **120% w/v**.

In Patterson's formula, **12 g of each salt** (copper and iron) are dissolved, giving a **12% concentration** for each reagent (corresponding to approximately **0.48 M** for copper sulfate and **0.45 M** for ferric ammonium citrate).

The **total concentration** of the mixture equals the sum of its individual components: **12% + 12% = 24% (~0.93 M)**.
If one were to increase the amount of copper sulfate in the sensitizer, the margin for addition is quite small: **31% – 24% = 7%**, and this value would be halved if the ferric ammonium citrate were increased proportionally.
In other words, raising the copper sulfate from **12 g to about 15.5** g would introduce **more problems than benefits**.

Given the concentration of the salt, the paper would tend to absorb only the **water** from the solution more readily: the sulfate would **crystallize on its surface** before being able to penetrate the fibres, an occurrence that would compromise the success of the print. Patterson did his calculations well.

If needed, the copper content **could not be increased** simply by adding more copper sulfate. In contrast, there is a much wider margin of adjustment with **ferric ammonium citrate**: its amount could be increased more than **fourfold**.

An Alternative Source of Copper

When thinking of a **soluble copper source**, copper sulfate is the most obvious choice: it's cheap, widely available, and a staple of any laboratory or darkroom.
But this apparent simplicity is somewhat deceptive.
As already mentioned, the **molecular mass** of $CuSO_4 \cdot 5H_2O$ is **249.68 g/mol**, of which only **65.54 g/mol** correspond to **copper (Cu)**—the remaining **184.14 g/mol** are oxygen, sulfur, and hydrogen.
Thus, copper sulfate contributes only 26.21% pure copper, meaning that **three-quarters of its mass plays a marginal—or even negative—role** in the sensitizer. For a **more efficient cuprotype sensitizer**—one with improved photographic performance—an **alternative copper source** is needed.
Such a compound should satisfy three essential criteria:

1. **Greater solubility** in water.
2. **Higher intrinsic copper content** than copper sulfate.
3. Containing **photoactive and useful ions**.

The most promising candidate is **Copper(II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$)**.

Copper(II) chloride dihydrate
$CuCl_2 \cdot 2H_2O$
Synonyms:
Cupric chloride dihydrate
Copper dichloride dihydrate
Copper(II) chloride hydrate

Fig. 3.1 — Copper(II) chloride dihydrate is a hygroscopic and deliquescent salt — it absorbs water from the surrounding atmosphere. It should be stored tightly sealed in its container.

This salt has a **molar mass of 170.48 g/mol** and a **copper content of 38.44%**.
Thus, **for equal weight**, copper chloride provides **almost 50% more copper** than copper sulfate, while being **more than twice as soluble**.

Its **fine crystalline structure** also brings advantages in terms of **image resolution**.
Although **less economical** than copper sulfate, **Copper(II) chloride dihydrate** is still a **readily available and practical** alternative for photographic applications.

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.

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

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

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 lighter regions and a corresponding **loss of contrast and detail**.

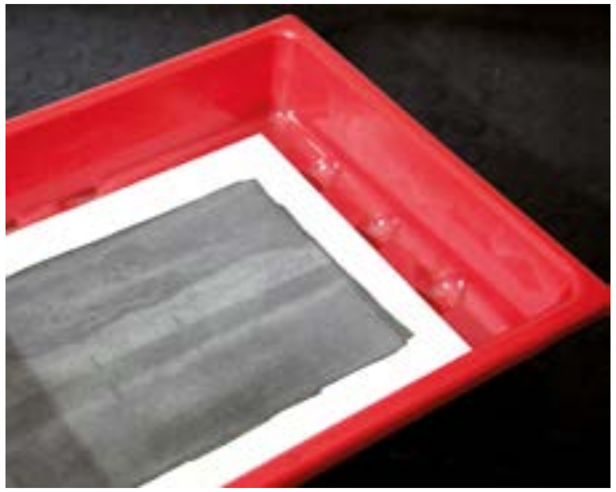


Fig. 3.7 — Proto-print obtained using a sensitizer with an imbalance between the copper supply and the photosensitive compound.
A negative image is created: the dark areas consist of copper(II) thiocyanate, and the light areas of copper(I) thiocyanate.
Exposure to humid air decomposes the former into 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** ($\mathrm{SCN^-}$) and the **cupric cation** ($\mathrm{Cu^{2+}}$) 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 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**.

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

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 **strong heat sources**—including **direct sunlight**—must be avoided.

Fig. 3.8 — The image obtained with the "Carminio" chloride method, on the same paper, appears in a more vivid red hue than that obtained with Patterson's method, and shows higher density and contrast.

Pigment *vs* Alkali

As already mentioned, the pigment of the **cuprotype** is a substance that is **very stable in air** and **resistant to dilute** acids. **Alkaline solutions**, however, alter it.

According to **Williams (1915)**,[5] when **cupric ferrocyanide** (in pure form) is subjected to the action of a **hot, concentrated sodium carbonate solution** (60-70 °C), it transforms into a bright green basic compound, according to the reaction:

$$Cu_2[Fe(CN)_6] + Na_2CO_3 \longrightarrow CuNa_2[Fe(CN)_6] \cdot CuO + CO_2$$

If the temperature is raised above **80 °C**, the pigment first **decomposes**, forming **cupric carbonate**, which then transforms into **cupric oxide**, while **sodium ferrocyanide** passes into solution.

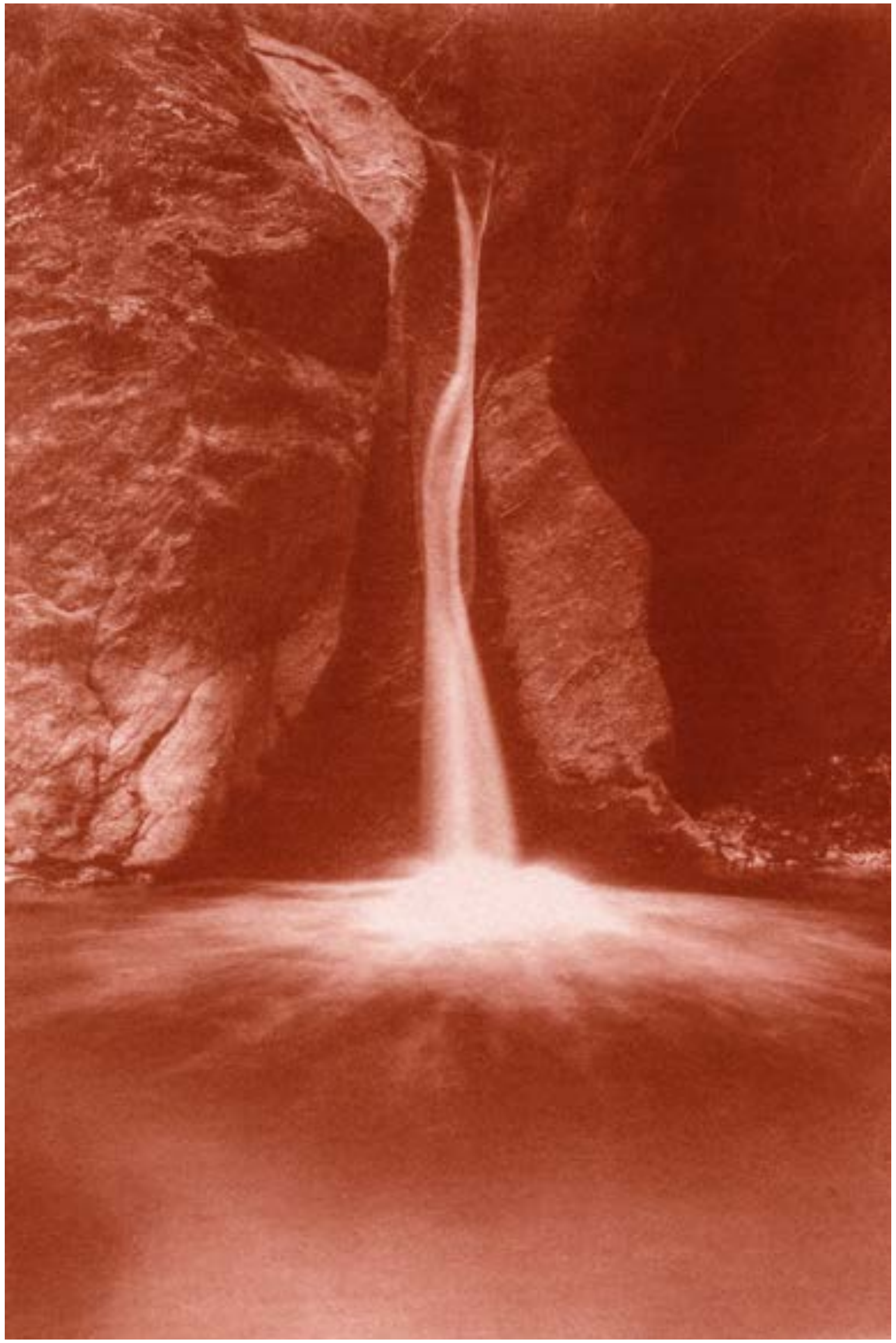
A similar basic compound can be prepared using **potassium carbonate**, but all attempts to prepare the corresponding **ammonium compound** in this way have failed. When **cupric ferrocyanide** is treated with **ammonium carbonate**, it is converted into a **double salt**, $Cu(NH_4)_2[Fe(CN)_6]$, which has a bright red color.[6]

What is stated above applies to **cupric ferrocyanide**, also known as **Hatchett's Brown**; however, it has proved to be **only partially applicable** to the **cuprotype pigment**, which is considerably **more resistant to alkalis**. This is because the **potassium–cupric complex** molecule already contains an **alkaline residue (potassium)** that is difficult to displace.
When a cuprotype print is treated with a **hot solution of sodium or potassium carbonate**, a **relatively rapid weakening** of the image occurs, yet without the immediate formation of the green compound. Instead, this color appears later, and **unevenly distributed** across the surface.
Only the **densest** areas of the image are converted, while the remaining portions are initially **bleached**, later gradually regaining a **pinkish-red hue**.

This behavior can be explained by hypothesizing that:

- The pigment is first transformed into **cupric carbonate** (or a coordination compound containing it), with the simultaneous formation of **potassium ferrocyanide** in aqueous solution:

$$2CuK_2[Fe(CN)_6]_{(aq)} + K_2CO_{3\,(s)} \longrightarrow CuK_2[Fe(CN)_6] \cdot CuCO_{3(s)} + K_4[Fe(CN)_6]_{(aq)}$$



IV

Water!

Among the bromides, ammonium bromide appeared to be the most suitable. This salt shows greater chemical compatibility with the other components of the photosensitive solution: the **ammonium cation** (NH_4^+) is already present by virtue of the ammonium iron(III) citrate; moreover, this choice avoided the excessive proliferation of cations from different chemical species, such as potassium and sodium (K^+ and Na^+),within the sensitizer.

A Simplified Process

In light of the above, the preparation of a new, **single-solution sensitizer** for cuprotype printing can proceed. A **2:1 molar ratio** between **ammonium bromide** and **cupric chloride** has proven suitable.

It must be noted, however, that adding ammonium bromide to the sensitizer recipe is not merely a formal change; it alters the very **chemical process** that leads to the creation of the proto-print.

In both the Patterson and Carminio methods, the formation of the insoluble copper salt—**copper(I) thiocyanate**—occurs **during the developing and fixing bath** through reaction with the **thiocyanate anion** (SCN^-) supplied by ammonium thiocyanate. In this simplified process, the thiocyanate is replaced by the **bromide anion** (Br^-).

In this case, however, the bromide anion does not act during the developing and fixing stage as in the two methods previously described: here, Br^- is already **present in the sensitizer**.
As a result, after exposure, obtaining the **insoluble copper salt—cuprous bromide (CuBr)**—requires only one thing: **water**.

The developing and fixing bath therefore consists simply of **water**.

> Using the bromide ion not only simplifies the developing and fixing phase of the proto-print but also removes the need for **ammonium thiocyanate**, a compound which—though not highly hazardous in the low concentrations used in cuprotype—is nevertheless potentially harmful to both health and the environment.

What can be done with bromides cannot be done with thiocyanates, since **thiocyanates cannot be included in the sensitizer formulation.**
As previously shown, the thiocyanate anion reacts with cupric ions (Cu^{2+}) to form copper(II) thiocyanate, an insoluble black precipitate:

$$Cu^{2+} + 2SCN^- \longrightarrow Cu(SCN)_2 \downarrow$$

This black compound decomposes in moist air to yield **copper(I) thiocyanate**, a white solid, nullifying the desired photochemical reduction of copper during UV exposure.

In short, the same salt would form both in the UV-exposed and unexposed areas of the print, resulting in a **flat image almost entirely devoid of detail**.

Fig. 4.1 — The cupric ion reacts with a solution containing ammonium thiocyanate, forming cupric thiocyanate, an unstable black precipitate.

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 that is too moist prevents the possibility of obtaining a high-quality print. 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** of the sensitizer solution to the 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.

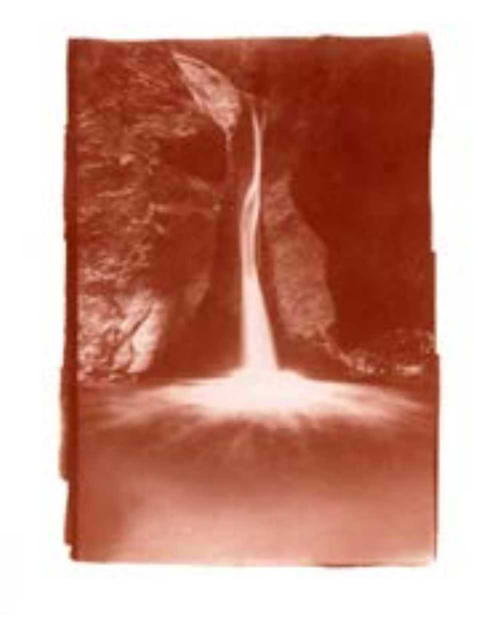


Fig. 4.14 — Print developed in plain water. Good contrast and bright highlights, but with little detail.

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

Toning Treatment

As has been learned by now, this treatment—the last one of a chemical nature—is the step that leads to the creation of the pigment in the cuprotype. It is at this stage that the almost invisible image of **cuprous bromide** is converted into a true **cuprotype**.
As in the case of copper(I) thiocyanate, **copper(I) bromide** reacts with the **potassium ferricyanide** solution, reducing the latter to **ferrocyanide** and oxidizing **copper(I)** to **copper(II)**. As a result, the insoluble reddish-brown precipitate of cupric potassium ferrocyanide is formed once again:

$$\mathrm{CuBr}\ \mathrm{(s)} + \mathrm{K_3[Fe(CN)_6]}\ \mathrm{(aq)} \longrightarrow \mathrm{CuK_2[Fe(CN)_6]}\ \mathrm{(s)}\downarrow + \mathrm{KBr}\ \mathrm{(aq)}$$

(s) = solid ; (aq) = aqueous solution

Technical / Chemical Material	Quantity
Potassium ferricyanide solution (p. 106)	1 L
1 L Glass or PET measuring jug	1
Plastic print tongs	1
Photographic tray (appropriate for print size)	1

Table 4.8

Procedure

Pour an appropriate volume of the **3% ammoniacal potassium ferricyanide solution** into a photographic tray and immerse the print, previously cleared of any residual iron salts. Agitate continuously for the first minute, then for 10-second cycles every minute thereafter.
Toning of images obtained with this sensitizer requires more time and should be stopped once the desired density is reached; in most cases, **20–30 minutes** are more than sufficient.

Operation	Mode	Time (minutes)
Agitation	Alternate	15–30

Table 4.9

Final Washing

The print is then washed under running water to remove all residual potassium ferricyanide—a crucial step in achieving a clean, stable image.
The washing time—**30 to 60 minutes**—depends on the type of paper used. Even slight yellowing will be clearly visible when the print is examined under transmitted or backlighting.
Potassium ferricyanide is **highly persistent** within the paper fibers; any yellowing indicates its presence, and washing must therefore be extended.

During this process, the **image density** may decrease slightly, and a **color shift** will occur—the exact hue depending on both the **paper type** and the **pH of the wash water**.

Procedure

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

Table 4.10

Drying

After adequate washing and confirming the **absence of ferricyanide 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 **strong heat sources**—including **direct sunlight**—must be avoided.

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.

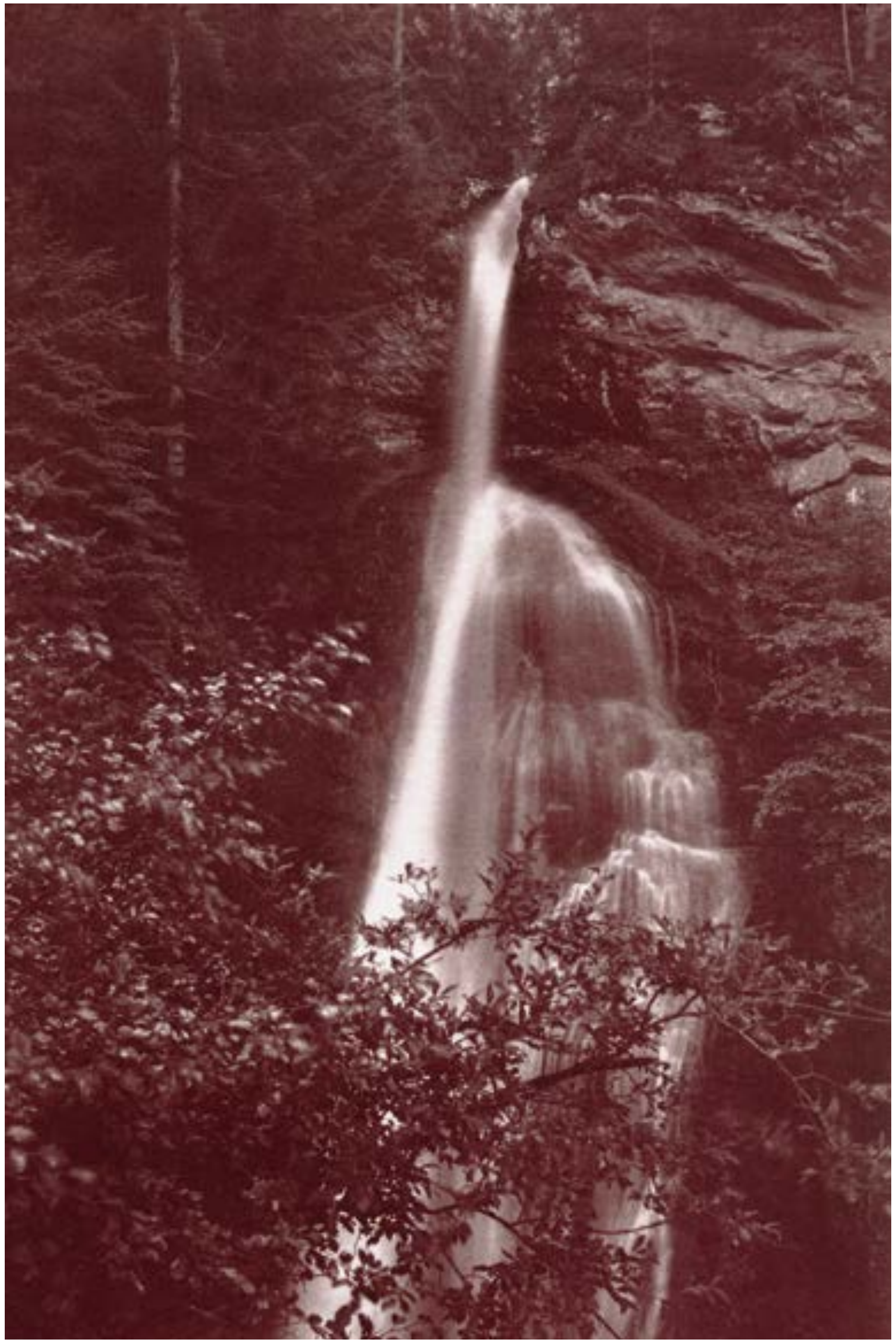
The best results are in fact obtained by adding a few milliliters of the sensitizing solution to the developing water or, alternatively, by introducing a small amount of a **mildly acidic iron salt: ferrous ammonium sulfate (Mohr's salt)** has yielded the most consistent results.

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

Page 134: *Cavalese Waterfalls*
Cuprotype print, Carminio process (toned with 10% potassium ferrocyanide), on Fabriano Unica paper (250 g/m²), iron-salt toned (Obernetter method).

The Obernetter Process

Except for the bromide-based process, all the work carried out so far on sensitizers originates from **Patterson's formula**, which itself is derived from that of **Obernetter**[1]—whose original recipe has not yet been presented.
It is considered more useful to first become familiar with modern methodologies before analyzing with greater awareness an old printing process that still retains uncertain aspects.

The information relating to this formula appears in the May 27, 1864 issue of The Photographic News, which published a translated version (from German into English) of an article by Obernetter himself, titled "*Positive Printing without Salts of Silver.*" The text is not very clear, and there are some inconsistencies in the description of the process; however, it is difficult to determine whether these are consistent with the original source cited—the *Photographisches Archiven*,[2]—which, unfortunately, could not be located or consulted.

The sensitizer formula and the main stages of the process are as follows:

> «Take the ordinary photographic paper, unsalted, and float it upon the following solution

Water	1000 parts
Solution of sesquichloride of iron (sp. gr. 1.53–1.6)[*]	13 parts
Crystallized chloride of copper	100 parts
Hydrochloric acid, pure and concentrated	12 parts

[* *Ferric chloride solution: density 1.53–1,6 Kg/L, corresponding to a concentration (m/v) of approximately 49% to 54%.*]

> The paper is allowed to remain two minutes on this solution, then drained, and hung up to dry.
> This operation may be performed by diffused daylight, without inconvenience.
> The properties of paper thus prepared are very remarkable.
> Two sheets, prepared two years ago, furnish now the same results as when recently prepared.

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.

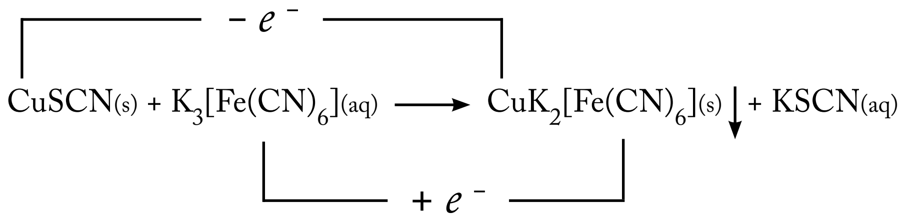
Potassium ferrocyanide
$K_4[Fe(CN)_6)]$

Synonyms:
Potassium hexacyanoferrate(II)
Yellow prussiate

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

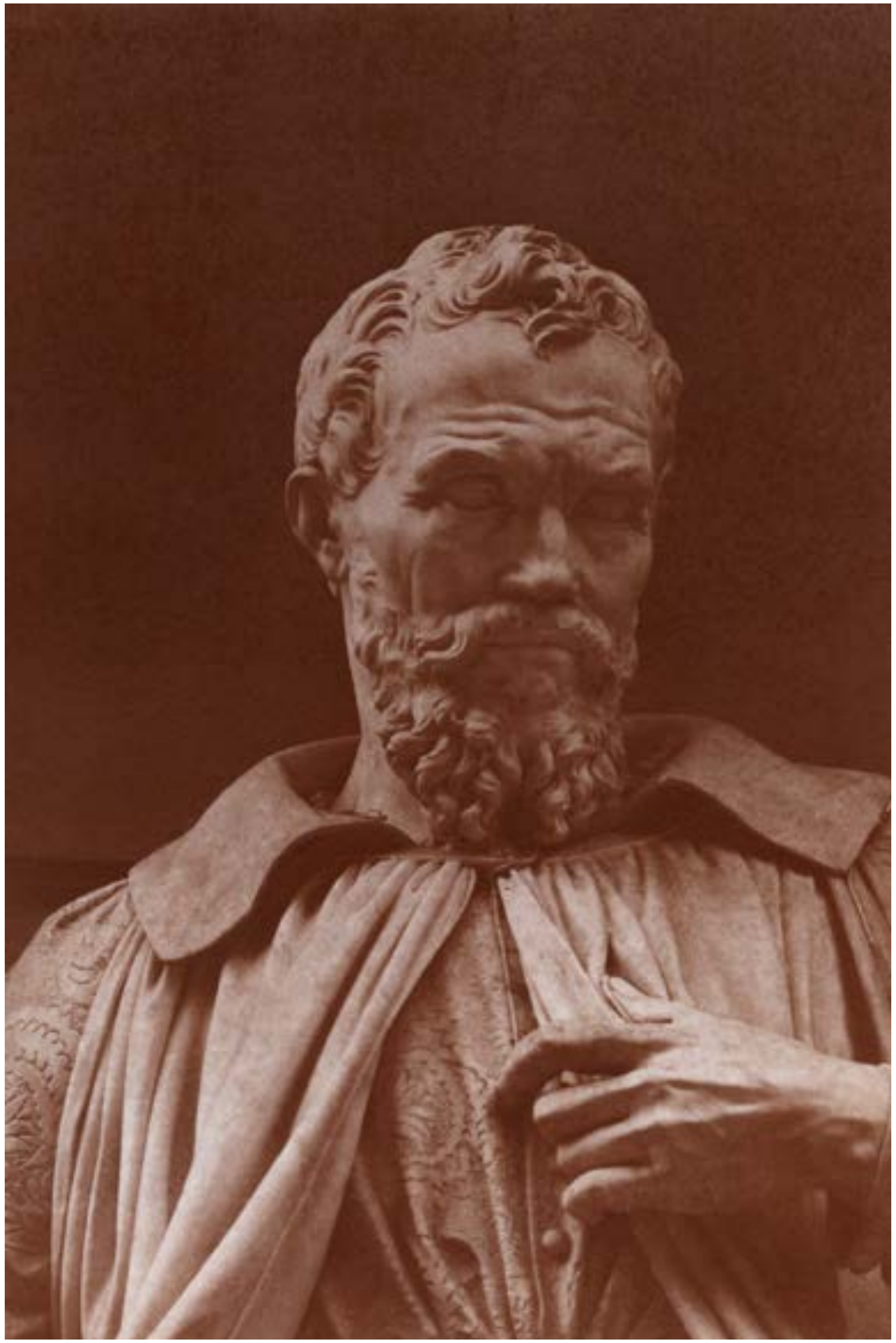
In the toning bath, the action of the two different reagents leads to distinct reactions, which, under ideal conditions, ultimately produce the same result.

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



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

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



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. 6.1 — Print treated in a 10% potassium ferrocyanide bath. After 2 minutes of immersion, the image is almost imperceptible.

Fig. 6.2 — Print removed from the ferrocyanide bath after 15 minutes: the image is barely visible and fades into the background.

Fig. 6.3 — Print after 5 minutes of washing: the image begins to separate from the background, and the color shifts toward lilac tones.

Fig. 6.4 — After 10 minutes of washing, the image density increases, and the color tends increasingly toward violet.

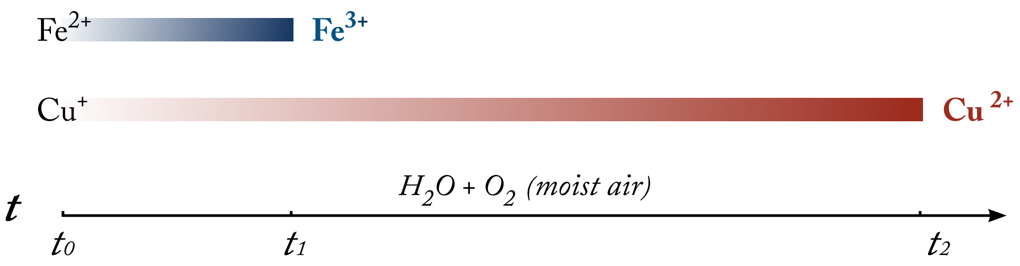
As can be seen from the images, **under ideal conditions,** the prints do not "take on a red tone that increases their intensity," as Obernetter wrote; rather, the tone becomes **lilac,** which gradually **shifts toward blue-violet** over time.
This latter phenomenon can be interpreted as the gradual oxidation of **Prussian white** into **Prussian blue** upon exposure to air.

According to **Mike Ware**[2], **Prussian white** (also known as Everitt's salt, Williamson's salt, or Berlin white) is an **insoluble, colorless salt** that is easily **oxidized by air** (or other oxidants) into **Prussian blue.** This compound forms through the reaction between the ferrous cation and the ferrocyanide anion:

$$\mathrm{Fe^{2+} + [Fe(CN)_6]^{4-}} \longrightarrow \begin{array}{c}\text{Prussian white}\\ \text{(air-unstable)}\end{array} \longrightarrow \text{Prussian blue}$$

The ferrous ions are realistically residues of the sensitizer trapped within the layer of **copper(I) thiocyanate deposited on the paper** during the initial wet treatment of the print—the development and fixing stage.
To avoid contamination from external iron sources, washing was carried out entirely with demineralized water.

The oxidation of copper proceeds more slowly than that of iron: the image begins to redden only after **Prussian white** has oxidized into Prussian blue. The typical reddish-brown color of the cuprotype appears after a few hours, at the end of the **spontaneous oxidative phase**.



The rate of oxidation varies depending on several factors, among them:

- the **type of sensitizer** used (residual impurities)
- the **age of the potassium ferrocyanide bath.**

A solution that has been previously used contains reaction products that accelerate the oxidation rate of both iron and copper. This rate can be further increased by adding a few milliliters of dilute hydrogen peroxide (e.g., 3%) to the washing water.

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+}.

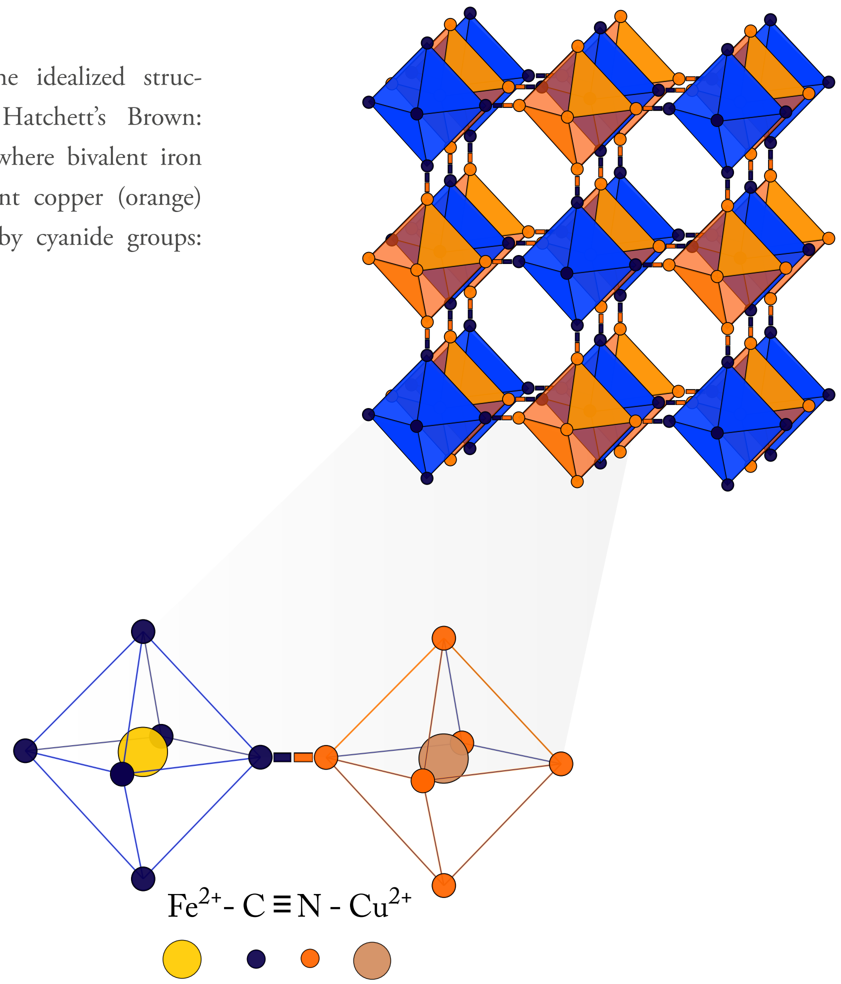
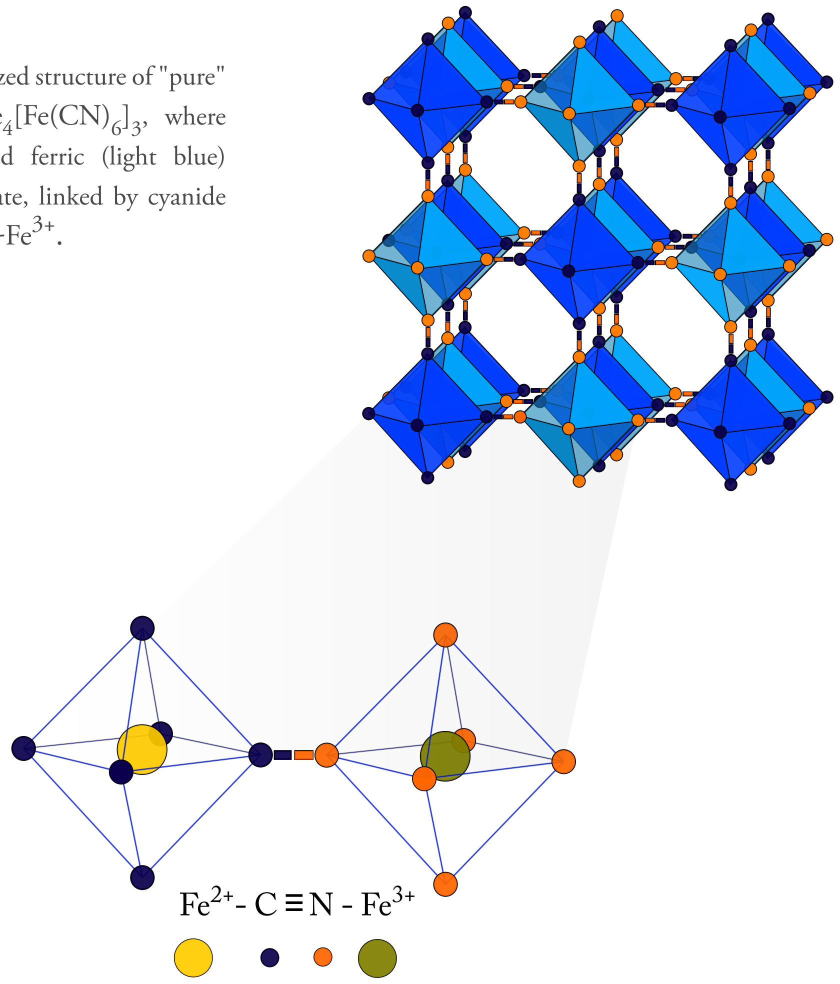


Fig. 6.19 — Idealized structure of "pure" Prussian blue: $Fe_4[Fe(CN)_6]_3$, where ferrous (blue) and ferric (light blue) iron atoms alternate, linked by cyanide groups: Fe^{2+}-CN-Fe^{3+}.



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.

Even though the ammonia concentration is very low (~1 part per 2000 parts of solution), there are free ammonium and hydroxide ions alongside potassium and ferricyanide ions.
In water, **potassium ferricyanide** $K_3[Fe(CN)_6]$ and **ammonium ferricyanide** $(NH_4)_3[Fe(CN)_6]$ virtually coexist:

$$3K^+ + [Fe(CN)_6]^{3-} + NH_4^+ + OH^- \rightleftharpoons 3NH_4^+ + [Fe(CN)_6]^{3-} + K^+ + OH^-$$

In laboratory conditions, substitution between potassium and ammonium ions in ferricyanide can indeed be achieved using **ion-exchange resins**.[14]
Whether this exchange can also occur spontaneously during the creation of the cuprotype pigment is difficult to say.
No sources have been found to confirm a reaction such as:

$$K_3[Fe(CN)_6] + 2NH_4OH + CuSCN \rightarrow Cu(NH_4)_2[Fe(CN)_6]\downarrow + KSCN + 2KOH$$

However, when the ammoniacal ferricyanide solution used for toning is left to evaporate, one first observes the crystallization of **ruby-red crystals of potassium ferricyanide** followed by a small mass of **yellow crystals**, very likely **ammonium ferricyanide**.

Fig. 6.21 — The ammoniacal ferricyanide solution, after evaporation of its aqueous component, leaves a saline residue composed of ruby-colored crystals of potassium ferricyanide (left) and probable ammonium ferricyanide (right).

The two substances were separated by exploiting their differing solubilities in water.

The solubility of ferricyanides depends greatly on the associated cation,[15] and ammonium salts generally show higher solubility than the corresponding sodium or potassium salts. **Flame tests** on the second crystalline substance confirmed the presence of the ammonium ion.

Fig. 6.22 — Flame test on potassium ferricyanide: the lilac color indicates the presence of the alkali metal.

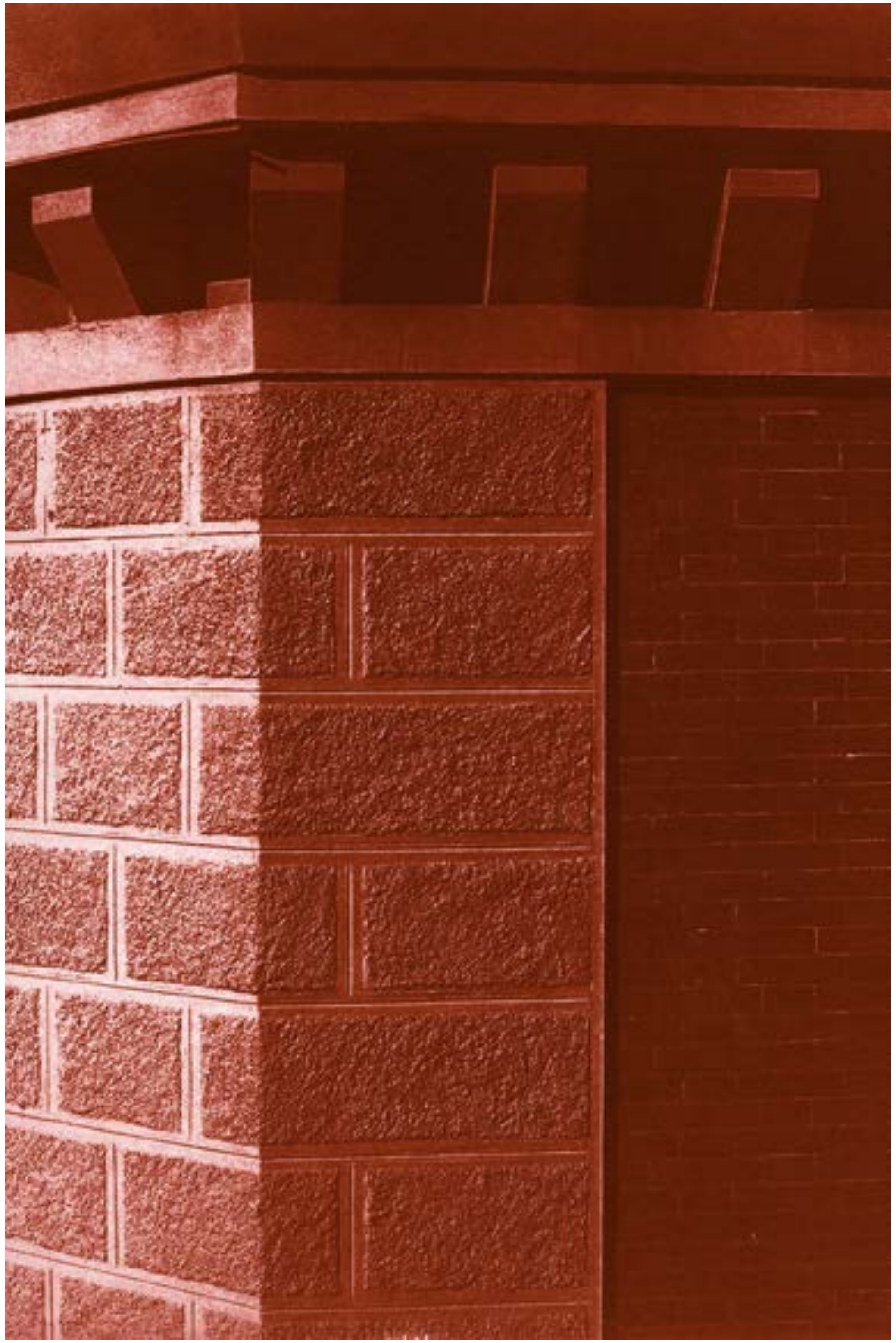
Fig. 6.23 — Ammonium salts decompose when exposed to flame, releasing ammonia.
The color observed in the flame test is a characteristic yellow-orange.

In *Treatise on Analytical Chemistry* (1916), Treadwell and Hall,[16] state that **cupric ferrocyanide dissolves in ammonium hydroxide,** producing the intense blue solution characteristic of the cuprammonium ion: $[Cu(NH_3)_4]^{2+}$.

In his article *The Action of Ammonium Hydroxide on Copper Ferrocyanide*,[17] E.D. Crittenden writes that when dilute ammonium hydroxide is slowly added to cupric ferrocyanide, the reddish-brown precipitate is completely converted into a **silky, dark brown solid**:

> «[...] probably a substance of the formula $Cu_2[Fe(CN)_6] \cdot 4NH_3$.»

This precipitate does **not** dissolve in concentrated ammonium hydroxide.



VII

Another Landscape:
The Hematotype

Pagina 166: *Solid horizons*
Cuprotype print, hematotype, on Fabriano Unica paper (250 g/m²).

The Echoes of Iron

Now that the main characteristics that distinguish the chemistry of the **cuprotype** have been analyzed as thoroughly as possible, it becomes clear how decisive —alongside that of copper—the **contribution of iron** is.
Its action is not limited to its fundamental role as a **photosensitive element**:

$$\mathbf{UV} \rightsquigarrow + \mathrm{Fe}^{3+} \longrightarrow \mathrm{Fe}^{2+}$$

$$\mathrm{Fe}^{2+} + \mathrm{Cu}^{2+} \longrightarrow \mathrm{Cu}^{+} \; (+\ \mathrm{Fe}^{3+})$$

Iron also plays a significant role in the **subsequent stages** of the process.
The **image density** increases according to the amount of iron present as an **impurity** within the structure of the proto-print; impurities that, after a series of **progressive oxidations**, lead to the formation of **ferric hydroxide**.
In the case of a **toning bath with ferrocyanide**:

$$\text{a)}\quad \textit{ferrous ions + ferrocyanide ions} \longrightarrow \textit{Prussian white}$$

$$\text{b)}\quad \textit{Prussian white} \xrightarrow{(+\,H_2O + O_2)} \textit{Prussian blue} \xrightarrow{(+\,OH^-)} \textit{ferric hydroxide}$$

With the **ammoniacal ferricyanide bath,** the reaction proceeds **more rapidly**.
Due to the **alkaline environment,** Prussian blue has a **very short lifespan** and is immediately decomposed into **ferric hydroxide,** which promptly integrates into the **image structure** together with the **ammonium-containing cuprotype pigment** (p. 164). The Prussian blue thus produced is the so-called **Turnbull's blue,** which is formed through an **immediate electron transfer**[1]: an electron moves from the **ferrous ion** to the **ferricyanide ion,** forming **ferric ferrocyanide**.

$$\text{a)}\; \textit{ferrous ions + ferricyanide ions} \longrightarrow \textit{ferrous ferricyanide (highly unstable)}$$

$$\text{a')}\; \underset{Fe^{2+} + [Fe(CN)_6]^{3-}}{\textit{ferrous ferricyanide}} \xrightarrow{Fe^{2+} \xrightarrow{e^{-}} [Fe(CN)_6]^{3-}} \underset{Fe^{3+} + [\,Fe\,(CN)_6]^{4-}}{\textit{ferric ferrocyanide}}$$

Prussian blue / Turnbull blue

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.

Process Stages

The materials may vary, but the general guidelines remain the same.
The only difference from the other processes previously described is the addition of an alternative toning treatment and a preliminary washing step:

1. Application of the photosensitive solution on paper (coating) and subsequent drying of the support
2. Exposure of the support to a UV light source (bromograph, UV lamp, or direct sunlight)
3. Chemical development/fixing treatment
4. Chemical clearing treatment
5. Chemical toning treatment 1
6. Chemical toning treatment 2
7. Washing
8. Drying

Coating and Drying

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

Under dim light conditions, spread the sensitizing solution evenly over the sheet, and allow it to dry, following the same procedures described for the other processes discussed earlier (pp. 56–58).

This sensitizer does not present any particular difficulties; drying under normal environmental conditions is sufficient. The paper should be allowed to dry naturally until the coated area no longer appears wet. In this case, however, it is **not advisable to accelerate the process** using heat sources—the hematotype sensitizer requires some **residual moisture**.

> It should always be kept in mind that a **completely dry photosensitive** layer is ineffective (or only minimally effective) from a photochemical point of view: **a certain level of moisture must be maintained.**

It is advisable to expose the sensitized sheets as soon as they are dry, since their effectiveness tends to gradually decrease over time.

Exposure

With medium-density negatives and a strong UV light source of 30–35 W, this sensitizer requires exposure times of approximately 10–12 minutes.

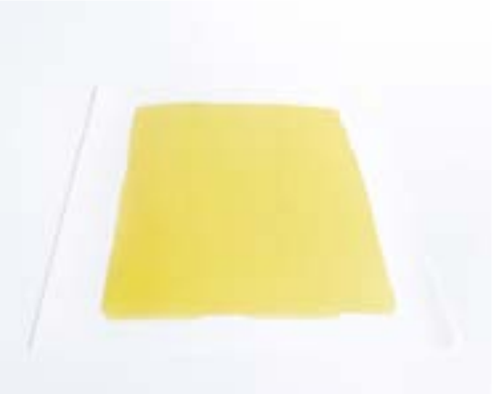


Fig. 7.6 — The dried sensitized sheet before exposure. The photosensitive layer appears bright yellow rather than green, as in the other formulations.

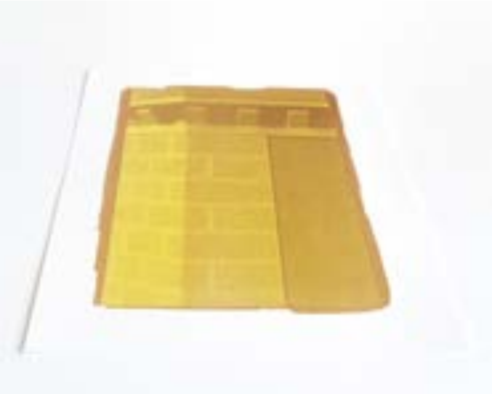


Fig. 7.7 — The sensitized sheet after exposure. The areas affected by light turn orange-brown, becoming darker in proportion to the intensity of UV influence.

Developing and Fixing

The next step is to transform the transient image into a permanent one.
To do this, the support is subjected to a **development and fixing treatment** aimed at producing a proto-print consisting of cuprous thiocyanate (CuSCN).

A treatment identical to that used in the **Carminio process** has proven perfectly suitable for this purpose. Its composition is recalled below:

Table 7.3

Chemicals	**Quantity**
Ammonium thiocyanate	12 g
Citric acid (anhydrous or monohydrate)	3 g
Purified/distilled water (to make up to)	1 L

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.

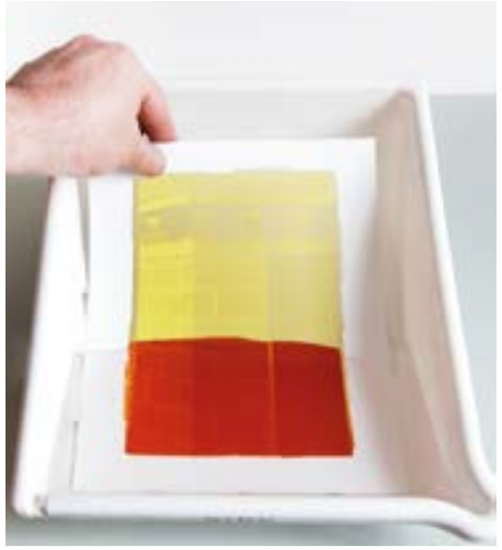


Fig. 7.8 — The sheet bearing the transient image immersed in the developing and fixing solution. Ferric ions react with thiocyanate ions, forming a compound of intense blood-red color.

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.

Toning Treatment I

In this treatment, the cuprous thiocyanate and the iron impurities incorporated within its structure react with an ammoniacal solution of potassium ferricyanide. At the beginning of this chapter, a plausible hypothesis was already outlined regarding what occurs during this stage; therefore, **no further theoretical explanation will be given**, and **the procedure and the results obtained are described below**.

Table 7.9

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

Table 7.10

Chemicals	Quantity
Potassium ferricyanide	30.0 g
Purified/distilled water (to make up to)	1 L
Ammonia solution (10%)	3.5-4.0 mL

Procedure

Proceed as usual:

- Fill a photographic tray with an appropriate volume of the ammoniacal toning solution and quickly (and completely) immerse the print. Agitation should be continuous during the first minute then for 15-second cycles every minute thereafter.

The total duration of the treatment may vary, depending on the amount of residual iron, from 5 to 20 minutes.

Table 7.11

Operation	Mode	Time (minutes)
Agitation	Continuous	5-20

Fig. 7.12 — The (wet) proto-print before the toning treatment. The iron impurities give the provisional image a gray-violet hue, much darker and more intense than usual.

Fig. 7.13 — The print after one minute of immersion in the toning bath. The image quickly takes on a deep, blood-red coloration, which is denser and more saturated than that achieved with the Carminio process.

Blood and Iron: The Hematotype

The defining characteristic of this new cuprotype process is undoubtedly its color: a **red** with a **deeper**, more **blood-like tone** than that produced by the *Carminio* and Patterson processes, both of which involve the removal of iron salts during the early wet stages.

The influence of iron on the density of the print is so significant that one might question whether the term cuprotype is still appropriate in this case. The color of the image results from a fruitful and intimate collaboration between iron and copper. Its sanguine tone defines its character so distinctly that it deserves a name of its own: **hematotype**, the *blood print*.[8]

The name clearly evokes both blood and iron — the iron oxide hematite (from the Greek for "blood stone")[9]—the mineral from which *Homo sapiens*, and before them the *Neanderthals*, produced the red pigments used in cave paintings. Hematite is also the main component (up to 70%) of **red ochre**, or *sanguigna*, a clay widely used during the **Renaissance and Baroque** periods to make drawing pastels.

Toning Treatment II

An alternative to the ammoniacal ferricyanide toning treatment can once again be derived from Obernetter's process.

This option is particularly suitable when the goal is **not** to achieve a red hue but rather a deeper, more **brownish**, iron-like one, either directly or as a base for subsequent chemical treatments aimed at modifying the hue.

Table 7.12

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

Table 7.13

Chemicals (Phase 1)	**Quantity**
Potassium ferrocyanide	100 g
Purified/distilled water (to make up to)	1 L

Table 7.14

Chemicals (Phase 2)	**Quantity**
Plain water	1 L
Hydrogen peroxide (3% solution)	20–30 mL

Procedure

In the **first phase** of the treatment, proceed as usual:

- Prepare a photographic tray with the 10% potassium ferrocyanide toning solution, and quickly (and completely) immerse the print. Maintain constant agitation during the first minute, then agitate for 15 seconds every minute thereafter.

The total treatment time may vary depending on the amount of residual iron, ranging from **15 to 30 minutes**.

Table 7.15

Operation	**Mode**	**Time** (minutes)
Agitation	Alternating	15–30

In the **second phase**:

- Transfer the print into a photographic tray filled with the hydrogen peroxide solution, and agitate continuously until the desired shadow density is reached.

The increase in image density is due to the rapid oxidation of Prussian white into Prussian blue (see Chapter VI), which temporarily dominates over the copper-based pigment of the cuprotype.

Table 7.16

Operation	**Mode**	**Time** (minutes)
Agitation	Continuous/alternating	10–20

Fig. 7.14 — The print after 15 minutes of toning in a 10% potassium ferrocyanide bath. The magenta hue of the image results from the blending of the blue and red pigments involved.

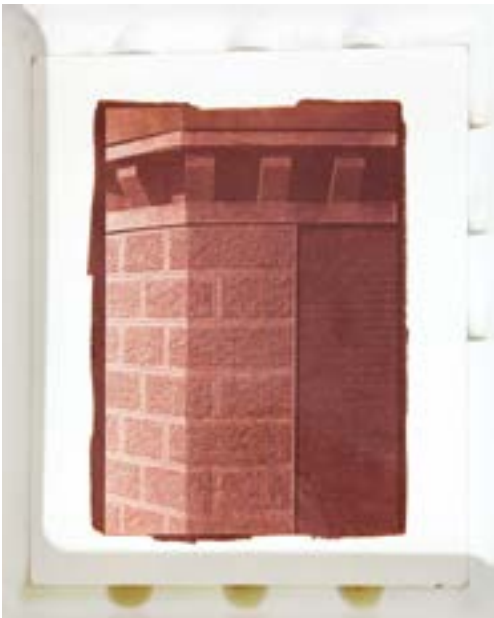


Fig. 7.15 — The print after 10 minutes of oxidation treatment. The Prussian blue has temporarily prevailed over the copper-based pigment, producing darker shadow areas.

Washing the Print

To obtain a high-quality and long-lasting print, it must now undergo a washing treatment intended to remove all residues from the toning bath.

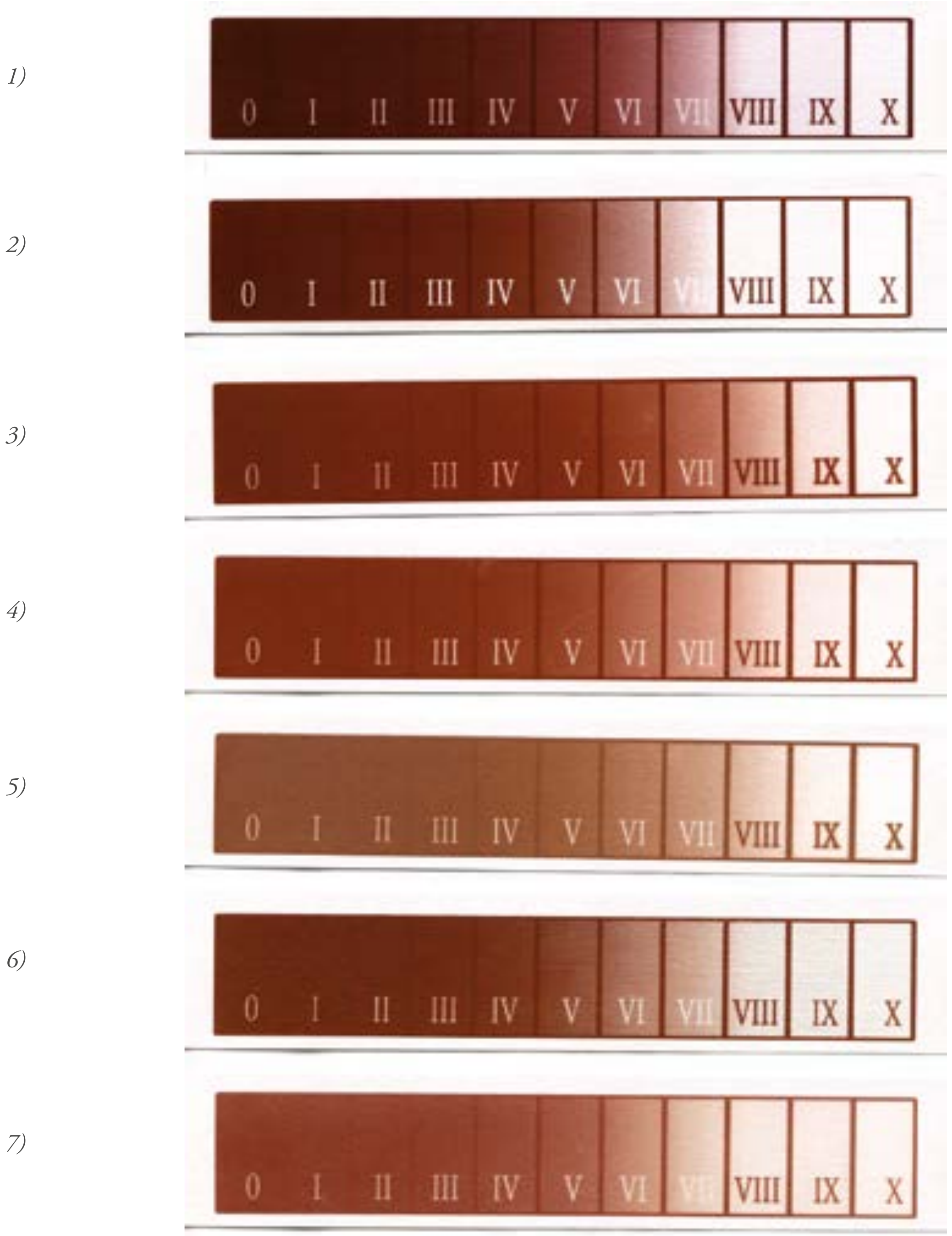


Fig. 7.20 — Scanned color test strips: *1)* Hematotype II, *2)* Hematotype I, *3)* Carminio, *4)* Patterson process with Carminio treatment, *5)* Patterson process, *6)* Bromide process developed with Mohr's salt solution (0.4%), *7)* Bromide process developed with water.

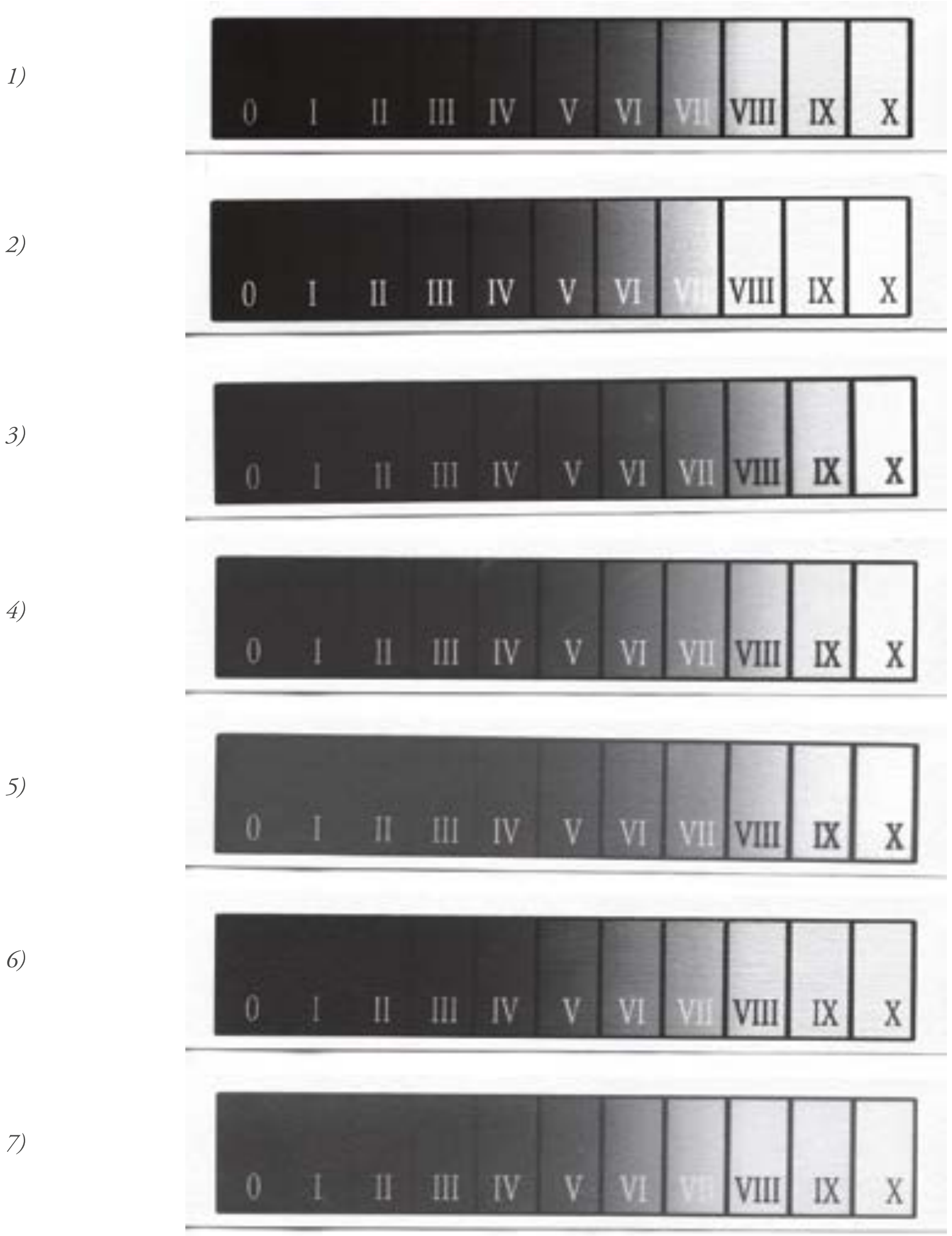


Fig. 7.21 — Scanned grayscale test strips: *1)* Hematotype II, *2)* Hematotype I, *3)* Carminio, *4)* Patterson process with Carminio treatment, *5)* Patterson process, *6)* Bromide process developed with Mohr's salt solution (0.4%), *7)* Bromide process developed with water.

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
6.5 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

Notes

1. Hunt's chromatype uses a copper salt, but the image substance is composed of a silver chromate (mercury, lead, or gold chromate, depending on the metal used).
   Burnett's process, which he named cuprotype, instead yields a final print composed of cupric ferrocyanide—more precisely, cupric potassium ferrocyanide. *(Author's note)*

2. Reply by Thomas Sutton, editor of *Photographic Notes*:
   «[...] 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.»
   (Source: *Photographic Notes* Vol. II, Thomas Sutton, Jersey (1857), p. 337.)

3. Duchochois P. C. (1891), *Photographic Reproduction Processes, a Practical Treatise of the Photo-Impressions Without Silver Salts*, pp.45-46

4. James Christopher (2020), *The Book of Photographic Processes,* 3 ed., pp. 555-558

Appendix

II

Brief Notes on Photochemistry

> 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 :

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

Cuprotype :

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

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.**

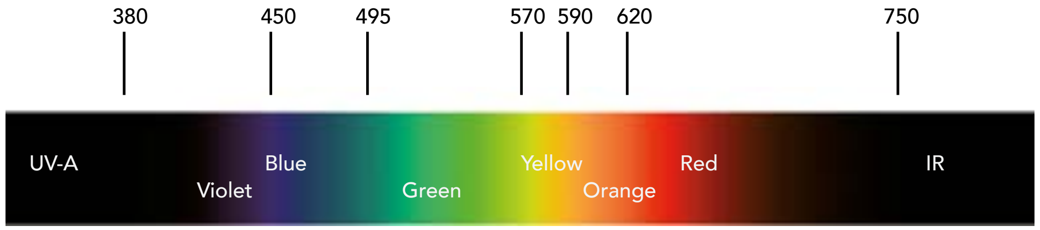


Fig. A2.1 — Electromagnetic spectrum ranging from the near ultraviolet (UV-A) to the near infrared (IR)

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]

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)