Citrate Copperplate Photogravure

Introduction : theorical principle of the use of Chiba System the Fenton reaction for copperplate photogravure

But what is it really?

The Fenton reaction is an oxidation reaction which consists of initiating decomposition reactions of molecules peroxidized by metal salts, in order to generate free radicals. These peroxidized molecules are variable: they can be hydrogen peroxide, sodium persulfate, ammonium persulfate, etc. In the presence of certain metal salts, peroxidized molecules (here H^2O^2 hydrogen peroxide) produce a highly reactive and unstable free radical hydroxyle **HO°** (due to a free electron on an external layer).

It is this highly reactive radical which will serve to initiate the gelatin polymerization reaction in the application we're concerned with.

In this case, we're using a ferric ammonium citrate (FAC), which is reduced to a ferrous salt (II) under UV light. This ferrous salt (II) will dissociate the H^2O^2 molecule, creating free hydroxyl radicals **HO°** . These will initiate chain polymerization of the organic gelatin molecule, raising its melting point. And it's this property that we'll use to develop the images in hot water.

Sources :
to find out more about the Fenton reaction

to find out more about free radicals

to find out more about Chiba System

The molecule used is ferric ammonium citrate green CAS No. 1185-57-5

(iron citrate) [2Fe3 + + C6 H6 O72]- ---- UV light -------> **2Fe2**+ + C5 H6 O5 + CO^2 (ferrous (II) salts are created)
(hydrogen peroxide) [H2 O2] + Fe2+ ---------> **HO°** + OH + Fe3+ . (**HO° free radicals appear**)

free radicals initiate polymerization of the gelatin molecule M = Monomer (mer)
HO° + M -----> **HOM°**
HOM° + M ------> **HOM2°**
HOM2° + nM ----------> **HO(M)nM°**

This is a chain reaction that takes place where Fe II ions are found, in areas exposed to UV light. And the power of polymerization is proportional to the quantity of free radicals, which in turn depends on the dose of Uv rays received.

First step / Making an aqueous solution of FAC green form (ammoniacal iron citrate)

The same CAS Number indicates that there are two forms of this product: a brown and a green

form.
The brown form has 65% citric acid, 17 to 18% iron, and around 9% ammonia: it is extremely soluble in water, and even deliquescent. Light reduces it to ferrous salt.
The green form has 75% citric acid, 15% to 16% iron, and 7.5% ammonia. It is equally soluble in water. And it is more rapidly reduced to ferrous salt by light than the brown variety.
We're going to use this green form because it's more sensitive to light.

500 ml solution with 20% FAC green and PH 3 :

Weigh 100 gr of green FAC powder

Dissolve in approx. 300 ml demineralized water at room temperature. If foaming occurs following agitation, isopropyl alcohol can be lightly sprayed onto the surface of the liquid.

Correct PH by gradually adding 11% hydrochloric acid solution until PH 3. (11 ml at 11% were required in total).

Top up to 500 ml with demineralized water. Final PH check and labelling of the bottle, store in a dark place in the fridge.

The need for an acid PH of around 3 is justified by the fact that gelatin polymerized by free radicals is much more fragile than gelatin exposed to dichromates or DAS. Various scientific articles observe and note an optimum PH for the Fenton reaction of between 2.5 and 3.5 . The main goal is to obtain a gelatin layer (+ or - polymerized according to the UV light transmitted through the positive film) that is sufficiently solid to resist perchloride etching times averaging between 23 and 28 min.

Second step : Sensitizing a sheet of gelatin paper

The sensitization was done on Phoenix paper (in the future, we'll try to do the sensitization with home-made gelatin paper).
There are two ways of doing this: either in a tray or with a brush. The latter, using a brush, has several advantages.

As only the necessary quantity is withdrawn with a syringe, the 20% FCC solution is not altered and always remains at the same concentration, and never receives dust or paper fibres.

For a 15x20 cm copperplate, we'll sensitize a slightly larger gelatin paper (approx. 16x21 cm). Using a magnetic system, we hold the gelatin paper immobile in a tray. Using a high-quality soft brush with no metal parts (like those used in the cyanotype process) and approximately 20 ml of FAC 20%, apply the sensitizing solution for 2 min 45 sec.

Drying is then carried out by transferring the gelatinized paper, gelatinized side down, to a clean, degreased Plexiglas plate.

Depending on climatic conditions, temperature and humidity, the drying time may last several hours. This drying time can be greatly reduced if you have a closed cabinet with a fan and a desiccant, such as calcium chloride.

Third step :UV exposition

The process is the same as for chromium salts or Das.
But for images of the same density range, printed with the same material, here the exposure time is multiplied by more than 2.
With dichromate, it took 2 min, with Das 2 min 30 sec, and here with FAC, we need 5 min 35 sec.

These times were specified by successive exposure methods with different times, always using the same printer and the same UV exposure unit.

Fourth step / additional step: gelatin polymerization

The goal of this step is to produce free radicals to cause polymerization of the gelatin molecule to the point of changing its melting point. We need to use 0.3% hydrogen peroxide solution.

After many negative tests, I realized that the hydrogen peroxide solution rapidly lost its effectiveness after a few uses.
In fact, with time and repeated use, they become loaded with Fe III ions, which greatly slows down the production of free radicals.
A new 0.3% hydrogen peroxide solution is therefore required for each heliogravure.
For this reason, I use a concentrated 12% solution of H^2O^2 and, with a volume of 12.5 ml diluted in 500 ml of demineralized water, I obtain half a liter at 0.3%.

The solution can be heated to 25/30°C to enhance its action.

The polymerization bath requires 25 to 30 sec.

Fifth step: transfer to copper

The transfer of the gelatin to the copper plate does not differ greatly from conventional copperplate photogravure with other sensitizers.
Above all, the gelatin hardening process is less powerful.

To improve this transfer, the adhesion of the gelatin to the copper, it is necessary to either practice double exposure by exposing an aquatint screen, then the positive film, or to place an aquatint on the copperplate from the start of the process.

To improve this transfer-adhesion, I have seen the positive effect of a film of alcohol on the copper just before transfer. In this case, you need to find an aquatint that is not incompatible with alcohol. That's why I use asphalt for this aquatint.
In all cases, the copper plate must be completely degreased.

After transfer, the copper plate and gelatin paper are left to rest for around 12 minutes under a moderate weight, about 1.5 kg for a 15x20 cm plate.

Sixth step: Development and drying

This step is quite classic, and very similar to development with other sensitizers. The only real change is in the fragility of the gelatin layer that has to be deposited on the copper. With this sensitizer, which is less powerful than its predecessors (chromium salts, Das), the polymerized

gelatin is more fragile, and this must be taken into account during this operation. First of all, we need to find the ideal water temperature that will melt the non-insolated parts without damaging the lighter areas.

With bichromates, the ideal temperature for developing water is around 56°C. With Das, you need to stay at around 42°C. With citrate, 40°C seems to be sufficient.

Once the entire image has been developed, place the plate in a 75% ethyl alcohol bath for 1 minute and 30 seconds, stirring constantly. The alcohol absorbs the water contained in the gelatin layer, making it more solid.

Then dry the plate thoroughly in front of a powerful, cool fan to evaporate the alcohol remaining on the plate.

It's not a required option, but it is possible to harden the gelatin layer a little more. This can be done by placing the dried gelatined plate in an electric oven at a constant temperature of 80°C for 15 minutes. In this way, the gelatin will be even more resistant, and it will be possible to extend the etching time by a few minutes if necessary.

Final step: Iron perchloride etching

Here, we do exactly what we do in all heliogravure : we use successive etching baths with progressively more diluted concentrations of Perchloride (°B degré Baumé).

The first, more concentrated bath slowly etch the blackest or darkest areas, then move on to medium grays, reducing the °B until the highlights are reached.

The average time for an etching is between 23 and 30 minutes, but there is no hard and fast rule : the most important factor influencing etching is the temperature of the mordant baths, which can be influenced also by the temperature of the studio.

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Conclusion and observations :

This new sensitizer has a number of undeniable advantages when used in copperplate photogravure

Firstly, the non-toxicity of iron citrate, compared with dichromate salts. On this point, there can be no doubt. The components included in citrate's chemical formula, citric acid and iron hydroxyde, are known to be non-hazardous, and the ammonia solution used to manufacture FAC is in very small quantities. It should also be noted that this product is used in the food industry under the name E381, as an acidity corrector, a pH regulator, an anti-caking agent and an iron supplement in breakfast cereals. (It is also found in certain beverages and infant formulas).

The Das (diazidostilben), another sensitizer I've worked on, is also considered non-toxic, but its more complex chemical formula makes it harder to be certain, especially over the long term.

The second advantage of this product is its reasonable price, compared with that of Das.

The third positive point for this iron salt is that it is very easy to find on the market. In fact, in addition to its use in food, it is also used in several alternative photographic processes, in particular cyanotype. We can safely assume that this product will remain available for a long time to come.

What's more, there's a fairly simple method for making it yourself, but I haven't tested it yet.

Important note: although this product is not very dangerous, you still need to observe the usual safety precautions inherent in handling any chemical (gloves, glasses, etc.) and follow the rules set out in the safety data sheets for the chemicals in question.

This document is the result of several weeks of various attempts with this new photogravure sensitizer. There have been many trials and a number of failures.
All the many parameters that can influence the success or failure of a process involving many successive stages had to be researched and adjusted. Gradually, the results improved and, above all, became more and more reproducible. To my mind, this looks promising.

Nevertheless, I know from experience that I still need to make a few adjustments, which is why this document remains open to further modification, with the ultimate goal of making the process more feasible for photogravure printers, especially those who can no longer use bichromates or too expensive diazidostilbene .

After more than 11 years' experience in copperplate photogravure, I know that it's important to be modest, and that every copperplate photogravure to come is always a challenge, a field for experimentation and/or discovery.

Atelier Héliopse December 2023
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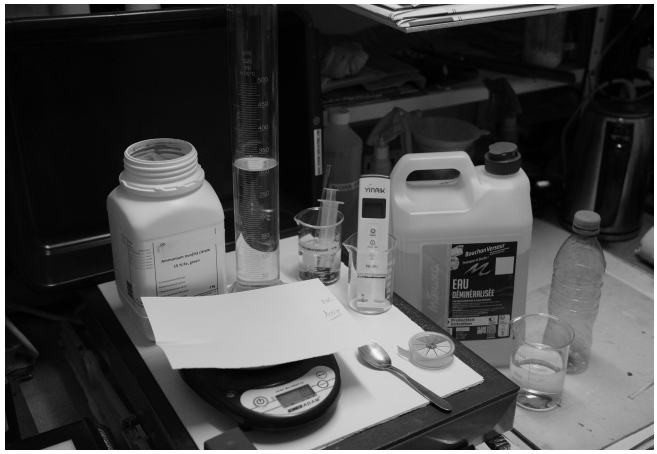
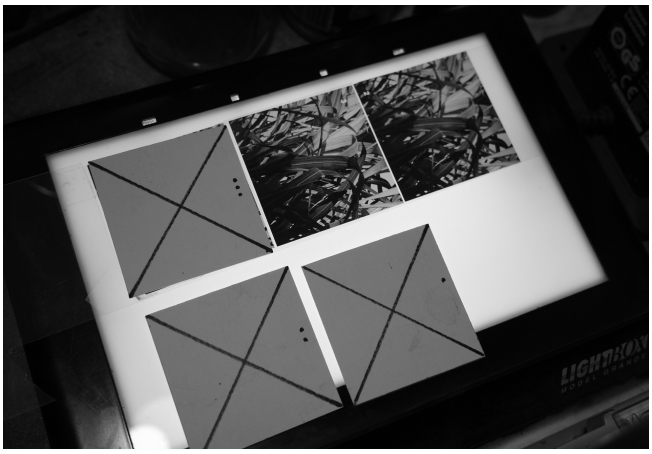
Illustrations



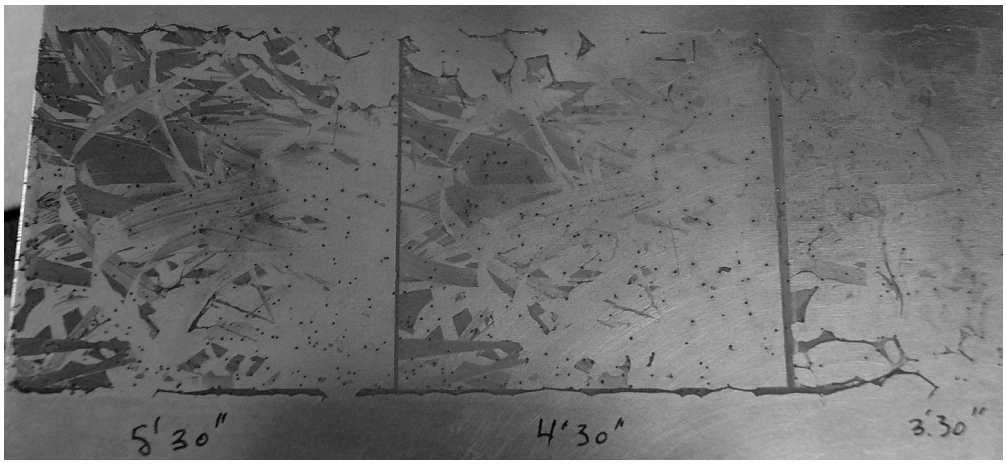
making solution FAC 20% ph3

adjusting ph to 3 with dilute acid solution HCL

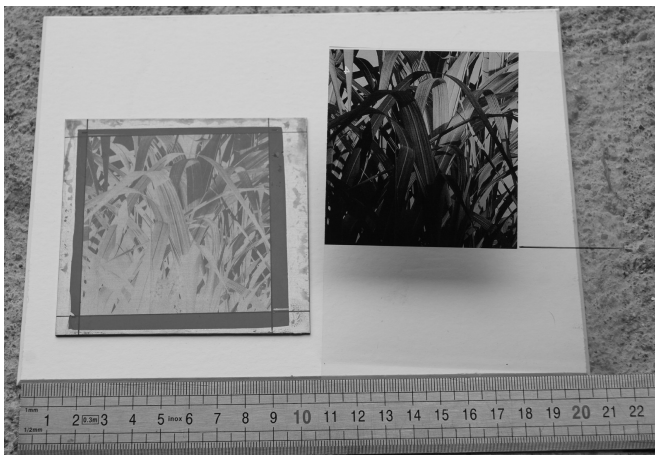
Phoenix Paper / brush sensibilisation



Searching for the ideal UV exposure time



UV exposure with 3 different exposure times



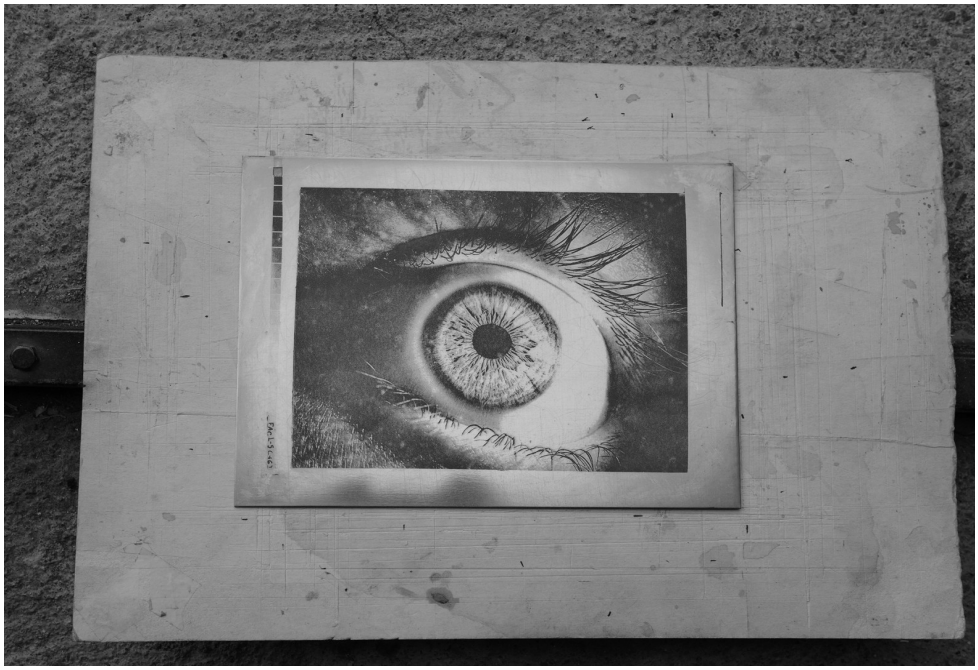
developed and stabilized gelatin on copper

Etched plate N°1 etching time 24'10" (46-43-41-40 °B)

Etched plateN°2 etching time 24'50" (46-43-41-40 °B)

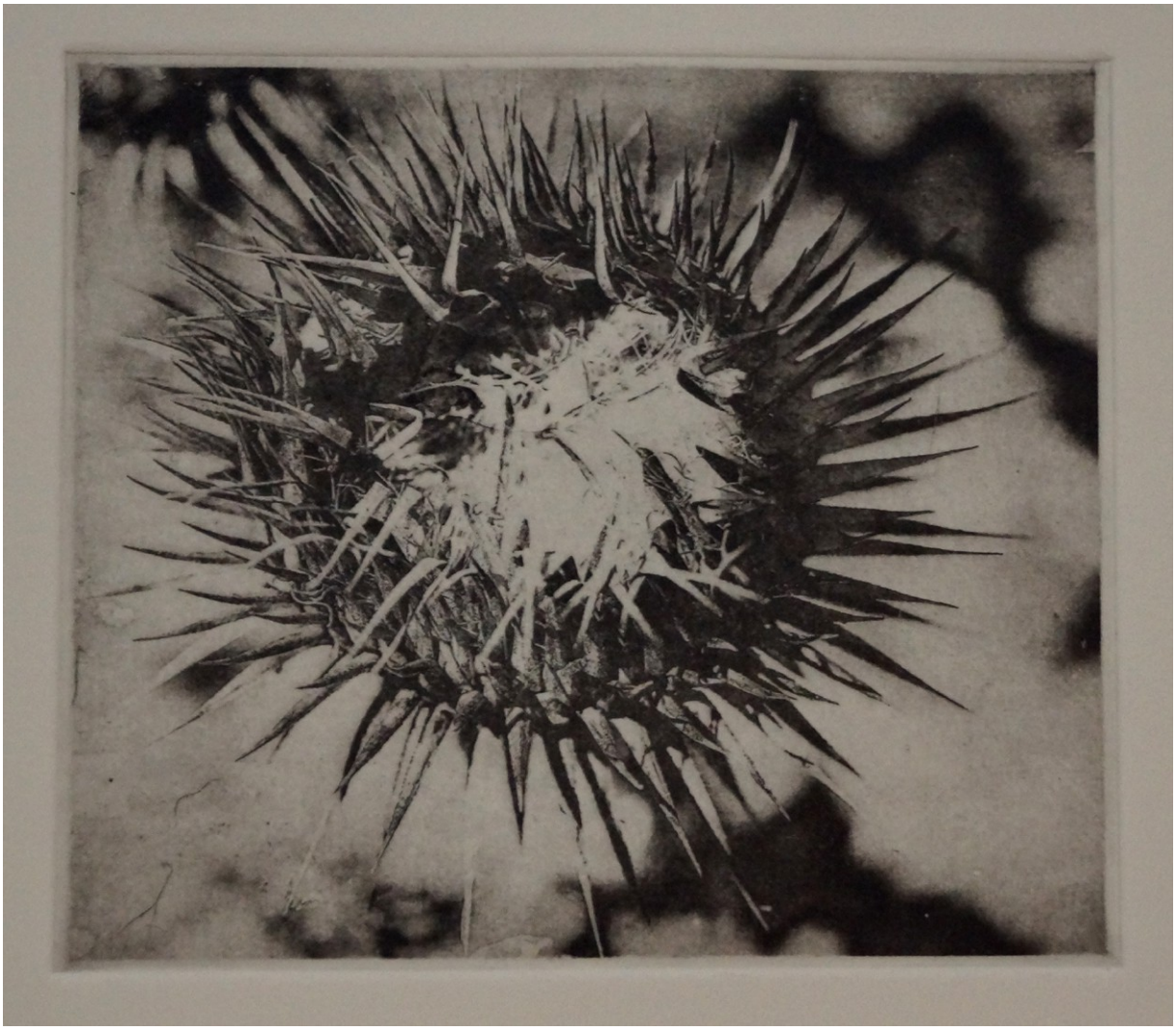
Plaque N°3 etching time 22'45" (42-41-40-39 °B

Plaque N°4 etching time 26'30" (41-40-39-41-42-43-39)



Plaque N°5 etching time 31'10" (42-43-42-40-39)

Impressions on paper 250 gr Clairefontaine Simili Japan
Inks Charbonnel Black 55981 & Raw Umber



with a little help from my cat