Short Treatise on Iron Salts
(fragments)

Followed by illustrated instructions
about how to make one's ferric oxalate

Pirrighelli's and Hübl's method
1883

Jean-Claude Mougin

♦ Proofs of the existence of God

" Sodium sulfite proves the existence of God " asserted Bob Schwalberg, a famous photographer and an amateur of sophisticated developers, because without a preservative there'd be no developer, no revelation and thus no proof of the existence of a divinity.

Niepce would have undoubtedly proved the existence of God with the asphalt of Judea, the natron with which people used to embalm their dead, Talbot with potassium iodide, Herschel with soda hyposulphite, Frederick Scott Archer with collodion, Poitevin with gelatin. And finally Willis, the inventor of the platinotype, would have proved God's existence with ferric oxalate, and we're going to do likewise.

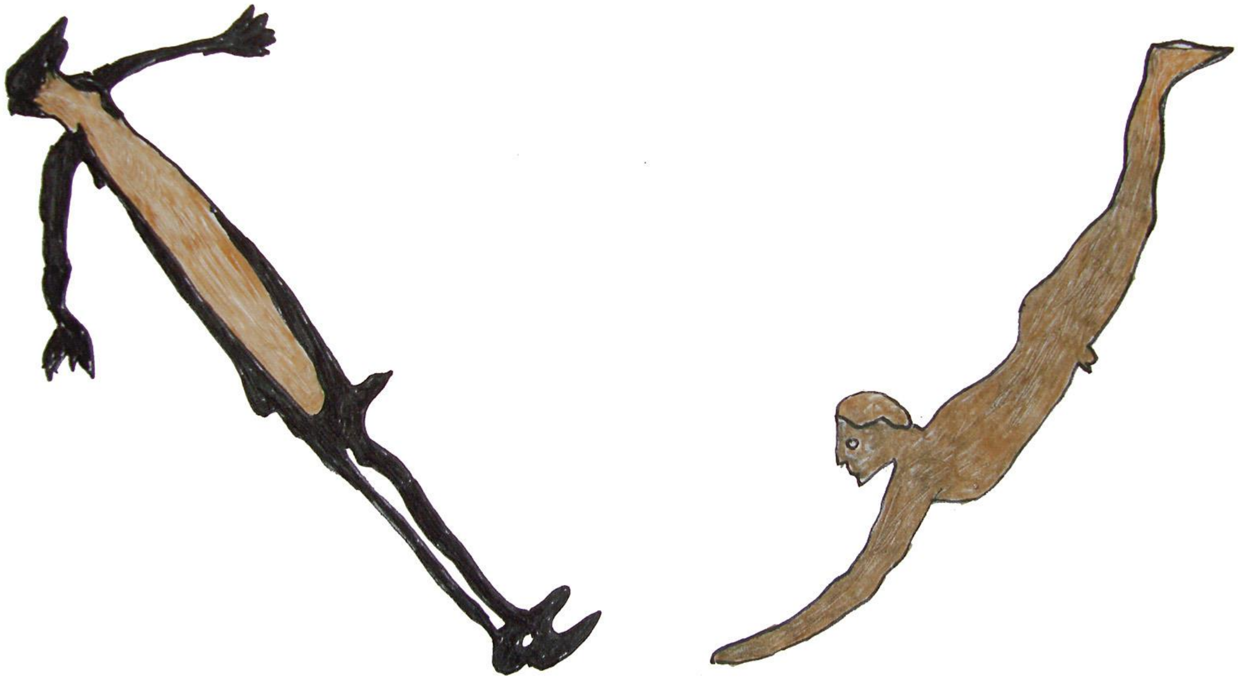
♦ And so long live siderotypie, and the siderotypists. We are indebted to Hershel the great physicist and astronomer, Talbot's friend, for the coining of the word sidérotypie, from the Greek " sideros ", to name the production of images from iron salts, and so it's sidérotypie that we're going to deal with in this treatise.

♦ Sidérotype and the birth of man

When he appeared 30.000 years ago, “homo sapiens”, expressed his new existence through religious attitudes and artistic manifestations. The first signs which he sent us through the ages were these negative or positive hands which he printed in the Chauvet cave, in those of Pech Merle, Cosquer, Cueva de Las Manos Pintadas in Argentina and in other places all around the world. Already man’s fascination for red ochres, and the fact that he mastered the techniques concerning iron oxides the color of which changes if heated, thus providing him with a full range of colors, turned him into a “spectator homo”: he started drawing and painting and then looked at images in which he discovered questions about his own existence. And so as René Char says: " before me, on the frieze of Lascaux, appears Wisdom – a fantastically disguised mother, with her eyes filled with tears ".

The man in the well in Lascaux cave with his bird’s head and in his sex sticking up, as well as the buffalo losing its bowels, both already stiff dead, are made out of these ochres which are variously colored iron oxides. 18 000 years later the diver in Paestum, in his graceful falls toward nothingness, with his sex floating through the air is made of the same materials.

Man has always lived in the Iron Age.



♦ Iron oxides and colors.

Red ochre, or the red from Mars, - the one with which the Yanomami warriors plaster themselves, the descendants of the Guarani, these new men " with no faith, no king, no laws " - , is, according to Montaigne, a red iron oxide. Among these red ochres, and redder still, there are the Venetian red, the Indian red and the English red.

When heated (or cooked) these ochres will give a " yellow of Mars ", the one that Poussin liked so much. It can become blue or purple when we add a polysulfure. If we heat it some more, we shall obtain burnt Sienna. Burnt Siena, red from Pouzzoles, from Ercolano, from Falun, Van Dyck’s red, flesh-colored ochre, macra, Armenia bowl, so many names pointing at so many colors which range from bright red to dark/deep black. If you study a painting by Caravaggio, or by

Rembrandt, you will travel through a Provençal Colorado, in which, among maritime pines, oxidized massifs rise, multi-colored, Mars yellow, Venetian red, burnt Sienna. …

And then everywhere rust, which is only an iron hydrate, eats into our cars, our balconies, our great tankers, our tanks. It destroys all this scrap out of which we built our mechanical civilization, the one before computers. Computers oxidize too as the data that their memories hold gradually fade away, in a misty sort of way , and they grow old and then die untimely just like the children suffering from " progeria ".

And nevertheless it’s out of this rust that the liqueur with emerald shades is going to be born : for the sidérotypiste, it’s like the Holy Grail, his or her philosopher's stone.

♦ " Nigredo ", the darkest black

For the alchemist, photographic processes doubtless have something to do with the Great Work, the raw material going through four stages. First we have the stage of blackness " nigredo ", then that of silver, then white, " albédo ", and finally red or "rubedo" from which the philosopher's stone will be born. This "stone" is a substance capable of achieving the transmutation of mean metals into gold or other precious metals.

All the processes with iron salts seem to follow this program, even if it has nothing to do with transmutation, but rather with revelation/developing. Iron salt supplies the image, then gold, silver, platinum, and uranium salts transform the iron image into golden, silver, even iron images which are called chrysotypes, kallitypes, platinotypes, palladiotypes, cyanotypes and many others: Herschel’s argentotype , Mercer’s chromatic photo, Philipson’s processs, Pellet print, Willis’s sépiaplatinotype, Colas’s ferrogallic process, Pizzighelli’s platinum printout, the ancestor of Bostick and Sullivan’s ziatype, Arnt and Cross’s Van Dick, Nakahara’s process, Jarman’s aurotype, Willis’s statista print.

To all those processes it is necessary to add the contemporary ones, the already mentionned ziatype, Mike Ware's new chrysotype, his new platinum, his new cyanotype, his argyrotype. (This list is given by Mike Ware in "Gold in Photography” and it’s bound to be incomplete)

♦ Iron salts and pharmacy

Following the invention of the calotype by Fox Talbot and its success – it replaced the daguerreotype and became the prototype of modern photography : with only one negative, one could get many prints - it was quickly noticed that the new pictures raised preservation problems, hence the idea of finding substitutes for silver nitrate among noble metals such as gold and platinum, later palladium.

After Obererierner’s disappointing tests (1780-1849) and those of Hunt (1844) on the sensibility of platinum salts, it was necessary to wait until Sir John Herschel managed to use the sensibility of iron salts in a convincing way with his first chrysotypes. He focused on iron ammoniacal citrate, which was a new substance in 1842, and which was used in pharmacy as tonic iron. Herschel went to London and consulted Dr Watson for stomach pains and the latter prescribed some Ferric Ammonio Citratis for him. This fact may indeed explain Herschell’s indifference for ferric oxalate, which didn’t seem to have healing qualities.

♦ Oxalate ferric or how to make some dough/money

In 1873 Willis was the one who invented and perfected the iron / platinum process but he protected it by taking out many patents so that the process could only be used industrially and for royalties. It explains why platinum then palladium then statista papers, were sold until 1930.

♦ Two mavericks : Pizzighelli and Hübl

The first one was a captain, the second a baron and a lieutenant, both officers in the Austrian army. It was a happy period then , when between two manoeuvres officers could devote themselves to amateur chemistry. And therefore they perfected a manual platynotypie process and published it in a book entitled " La Planotypie " which won the Voigtländer prize, namely a golden medal worth 100 ducats. In spite of the anger and threats of the Platinotype Company, this book was soon translated into English and into French and became sidérotypistes' Bible, and it remained so for a long time since Georges Tice used it in the 70s when he revived the process.

In French, in its February 1979 issue, the Swiss magazine Camera gave a complete description of the process by Carlos Richardson. Nancy Rexroth wrote a first complete article about iron salts in 1977: it was published as duplicated lecture notes by the Violet Press Company, in Yellow Springs. The adventure of the revival of the iron salts processes could begin.

By spreading the material that was necessary for these techniques, while working on the development of a new process named Ziatype, Bostick and Sullivan were going to insure the success and the sharing of these processes which have become not only alternative but also subversive in front of the overwhelming power of digital images.

" Everyone in front of their screen " such is new Big Brother’s slogan. “Everyone gets hold of their brushes and their sun lamps”, such is the new rebels’ slogan. Just as formerly diverse recipes for Molotov cocktails used to be handed round secretly, likewise will you be told here about the traditional but particularly effective way of making some ferric oxalate, very much similar to that of Pizzighelli and Hûbl in the past.

The workshop

♦ oxalate ferric: Shall we buy a kit or not ?

Today there are two ways of getting some ferric oxalate : either you buy some powder or a ready-made/an instant solution, at Bostick and Sullivan’s or Artcraft’s, or you make your own ferric oxalate. The simplest way is to follow the process given by Pierre Brochet during a workshop at the Niepce Museum in March 1983 and printed in the book(let) " Palladium " that one can download on the website "gallery-photo.com". (http://www.galerie-photo.com/platine-palladium_cours-2007.html).

Unfortunately this method requires the use of iron hydrate, a produce that all the big labs used to sell, and which today has disappeared from all their catalogs, so that now we have to make our own ferric oxalate

♦ Compared analysis of B&S ferric oxalates and ferric oxalate by Pizzighelli and Hübl (1983)

With the same negative, with a Stouffer 4X5 step tablet, with the same Crane's A811 paper, with the same spreading and drying techniques (spread the ferric oxalate on the sheet of paper with a brush for 2 mns, let it “stand” for 5 mns in the dark , dry it on both sides for 3 mns with a hairdryer). Then allow a 15 mns’ exposure to UV. And finally a " One shot " development : 60 cc of 11° sodium citrate plus 2 drops of 4 % Bichromate potassium, and clearing with a solution of oxalic acid and water (2 tablespoonsful of acid for 10 liters of water).

We can notice on this image that the gradation is approximately the same, on the other hand the density of the blacks shows big differences that we can measure with a densitometer, even if on the print above this difference is not visible.

♦ Measures of the ranges with the densitometer by transmission, 0 being measured on the white part of the paper.

	OxFe Pz & Hb	OxFe B&S
1.	2.37	1.83
2.	2.05	1.58
3.	1.65	1.55
4.	1.52	1.37
5.	1.31	1.17
6.	1.08	1.01
7.	0.84	0.85
8.	0.68	0.68
9.	0.58	0.58
10.	0.38	0.41
11.	0.32	0.35
12.	0.20	0.23
13.	0.16	0.19
14.	0.07	0.08
15.	0.04	0.04
16.	0.00	0.00

It seems that for two very close gradations, the homemade ferric oxalate has a density of pigments which is higher than what we get with the B&S ferric oxalate.

It even seems these aren’t quite the same chemical bodies. The first one is very clear with a very bright emerald green color, the second one is yellowish and a bit murky.

♦ There are several sorts of ferric oxalates.

This is what Mike Ware says in his "Chrysotype Manual" p. 139:

“The time-honored substance, used in several ferric salts processes such as traditional platinotypes and kallitypes, is iron oxalate. Unfortunately, this is yet another iron compound looked upon by chemists as being “ill-defined”. Different methods to make iron oxalate yield significantly different products; and although they all have the same formula (NH4)3 (Fe (C2O4)) 3H2O, this body is certainly not just a simple salt. It probably has a complex, oligomeric structure which remains unknown, because it has never been crystallized, and therefore never been subject to X-ray methods of structure determination.”

And likewise E. Trutat in his book « Tirages Photographiques aux Sels de Fer » published in 1904, distinguishes two forms of ferric oxalate: "You should only use pure yellow oxalate, a yellow and greenish powder insoluble in water, instead of the double ferric and potassium oxalate”. Then he gives instructions similar to those of Pizzighelli and Hübl, to those of Emery, and Pierre Brochet, and similar to the one that we are going to experiment here.

♦ Various techniques in order to make some ferric oxalate

These techniques are given in numerous books. Dick Steven's " Making Kallitypes, a definitive guide " is the most complete. He describes three methods which are the best ones, according to him. The first one uses ammonium ferric sulfate crystals and some ammonia. The second one uses the same ferric sulfate, but it reacts with some hydrogen peroxide, and the third one reacts with some potassium permanganate.

Oddly enough, the technique using some iron hydrate (obtained through the reaction of chloride iron with soda) is no longer mentioned. It is nevertheless the method given by the 2 founding fathers, Pizzighelli and Hübl, taken up again by Trutat, and by Emery, given by Pierre Brochet and which Christian Nze seems to have chosen. And so it means that we aren't going to describe anything new here but instead something that works very well and that will be explained thoroughly and carefully to whoever wishes to embark on an adventure which indeed won't take you beyond your kitchen where you'll have to follow the instructions of a recipe.

♦ Making iron oxalate from iron hydrate

HOW TO MAKE IRON HYDRATE

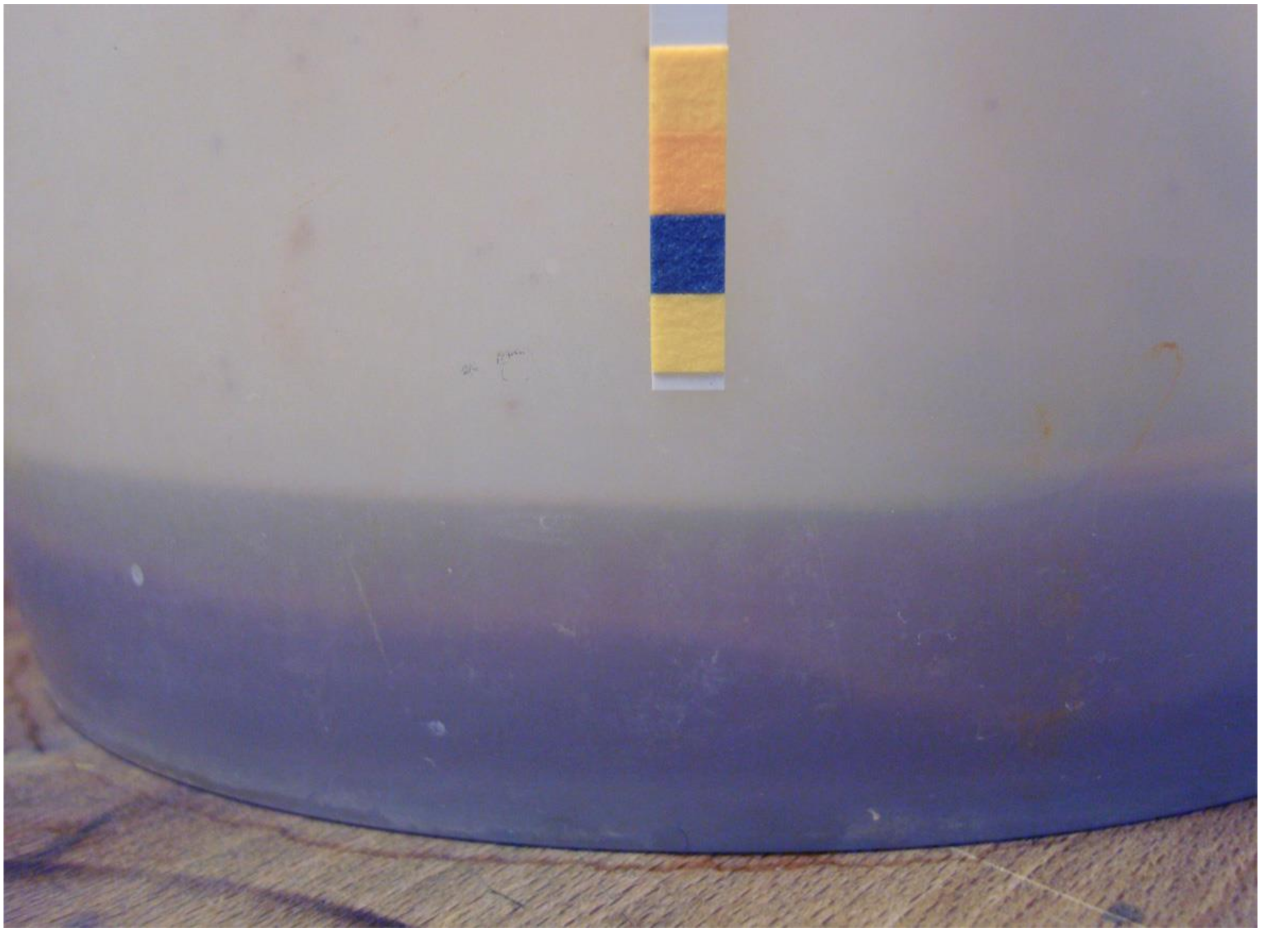
• What you need:

- an electronic balance (1/10th)
- iron chloride (iron perchloride) (in all stores dealing with engraving, 10$ kg)
- pearled caustic soda (in stores)

- a 10-liter bucket
- 3 nylon coffee filters (supermarket, plastic substitutes for coffee filters)
- paper coffee filters
- 3 one-liter containers on which to adapt nylon filters
- It’s highly recommended to buy a “Büchner vacuum-pump” worth 50$ (on Ebay, type « buchner pump »
- a portoir and 10 test tubes

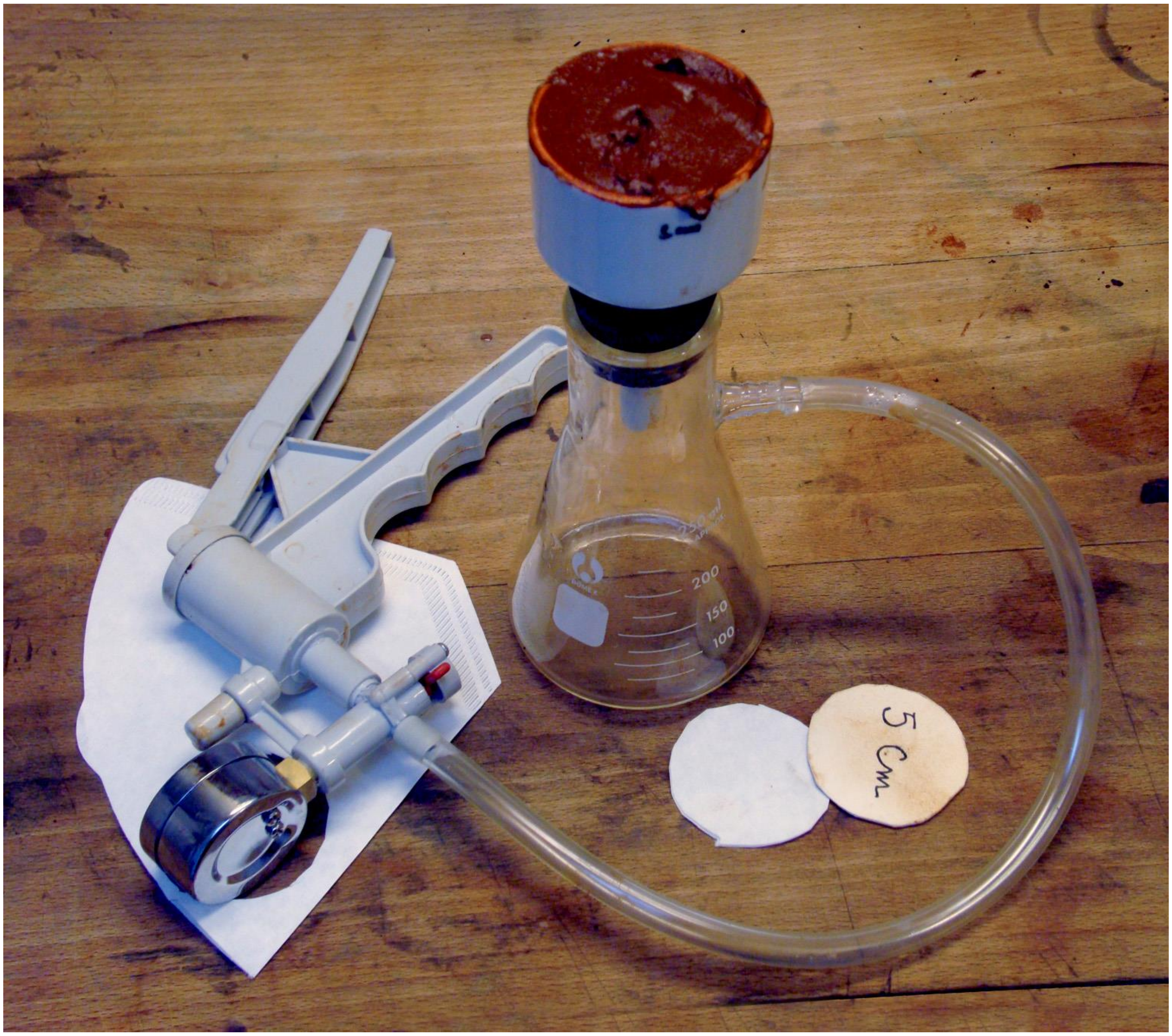
• **process**

- heat distilled water 500 up to 220° F.
- dissolve 50 gr of iron chloride, mix slowly, wear safety glasses
- add 25 gr of caustic soda, mix slowly (it's boiling), wear safety glasses
- put the mixture in a 10-liter bucket filled with warm water from the tap and let it stand for 15 mns (PH14). At the end of 15 mns, we can notice that the iron hydrate has settled at the botton.
- Siphon off as much clear water as you can but make sure you don't suck up the iron hydrate lying at the bottom of the bucket, so leave 2 or 3 cms of clear water.



- Repeat the same operation 5 times until the water has a neutral PH (pH7).
- After siphoning the water for the last time, place evenly the brown mass of iron hydrate onto the three coffee filters.

- At the beginning, stir from time to time to drain the iron hydrate and water mixture as much as possible. Let it drain for at least four hours, but this can last a whole night.



- It is important to eliminate as much water as possible, otherwise the ferric oxalate solution will be much too diluted. It is easier to add some water if necessary than to remove some.
- To do that, we use a Büchner funnel, consisting of a filter and a vacuum pump. We can find this equipment on eBay website (250 ml filtration flask / buchner pump tunne / vacuum) for $50.

- The 7cm filtres supplied in stores are too large : cut them down to 5-cm disks; you can use double thickness coffee filters. Wet the filter and stick it at the bottom of the porcelain funnel so that it blocks up its holes. Fill the funnel with iron hydrate and pump up to the 600 mark on the manometer. Wait till the manometer returns to zero. Do the same again with what's left of the iron hydrate.

♦ **How to make some ferric oxalate**.

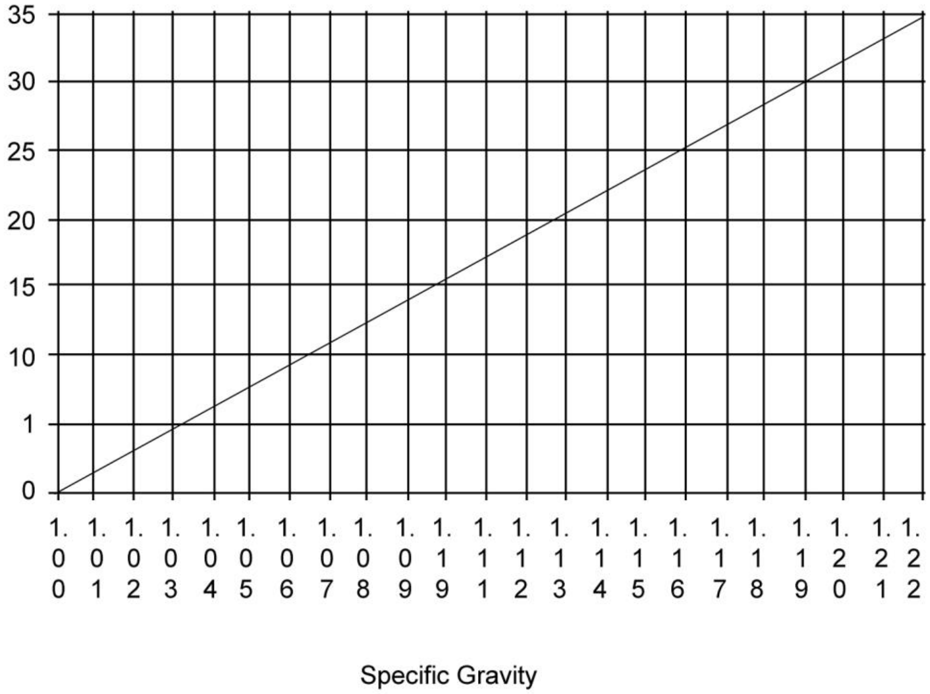
- Weigh 42 gr of oxalic acid for 100 gr of iron hydrate,
- Mix both ingredients (use a tungsten lamp, avoid natural light)
- Stir the mixture: it liquefies.
- Raise the temperature to up to 30° C (86 F), no more, in a bain-marie/double boiler; a higher temperature would transform the ferric into ferrous.
- Let it stand for one hour in the dark.
- Fill the clarification test-tubes. (At the bottom of the bowl there's some oxalic acid left: throw it away.)
- Let the mixture in the tubes settle for at least 4 hours, then ferric oxalate appears: it looks emerald green very clearly, separated from the iron that hasn't been reduced by the acid.

♦ Filtering the iron oxalate

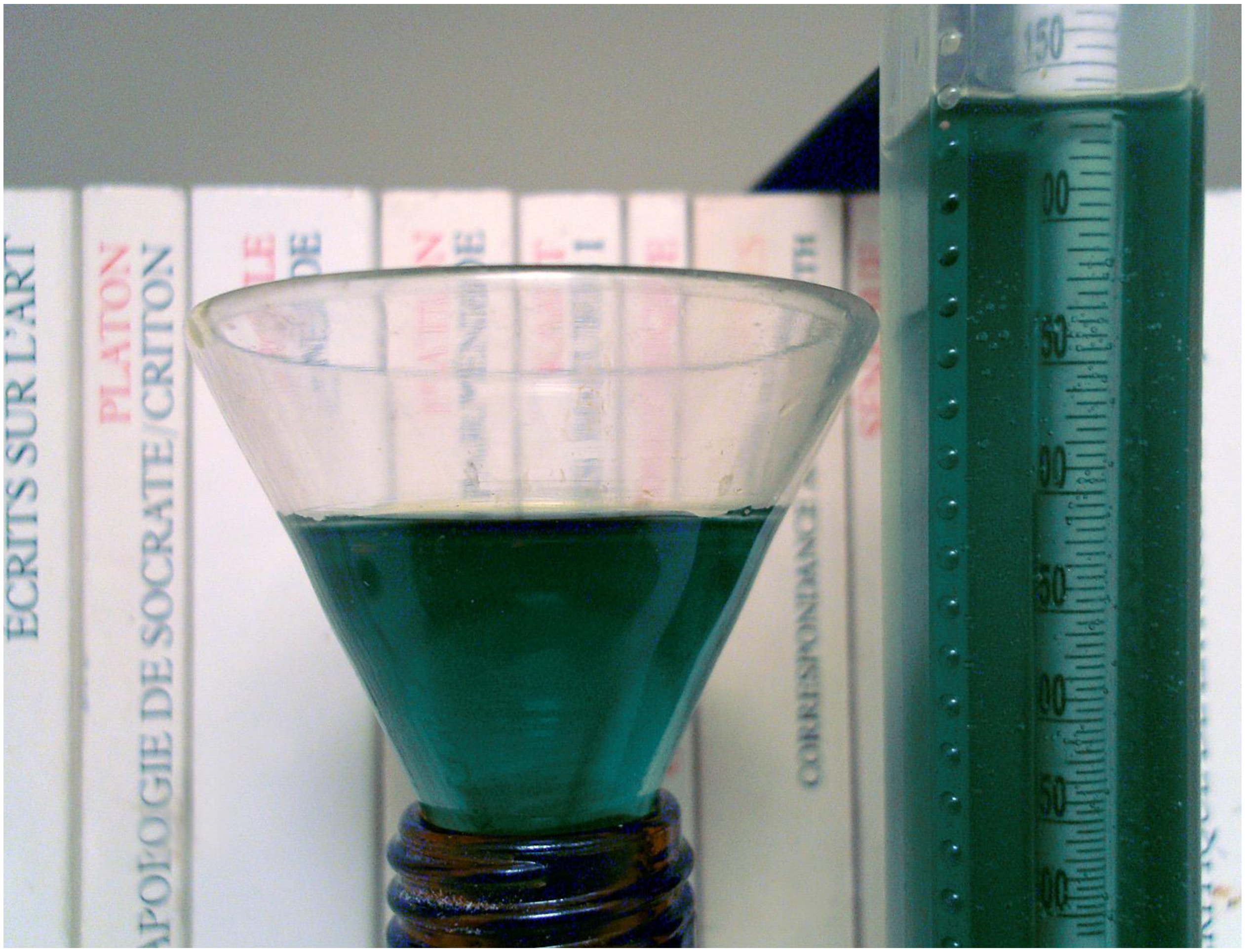
- Use a funnel the tube of which has been filled with some cotton wool.
- Filter several times, if necessary, until you obtain a crystal clear liqueur.

♦ How to determine the concentration of ferric oxalate

The percentage can be read on the specific gravity chart printed below



On this chart, we can read that for a 27 % concentration the coefficient of gravity is 1.17.



The simplest way of measuring this concentration is to use an aerometer as shown above.

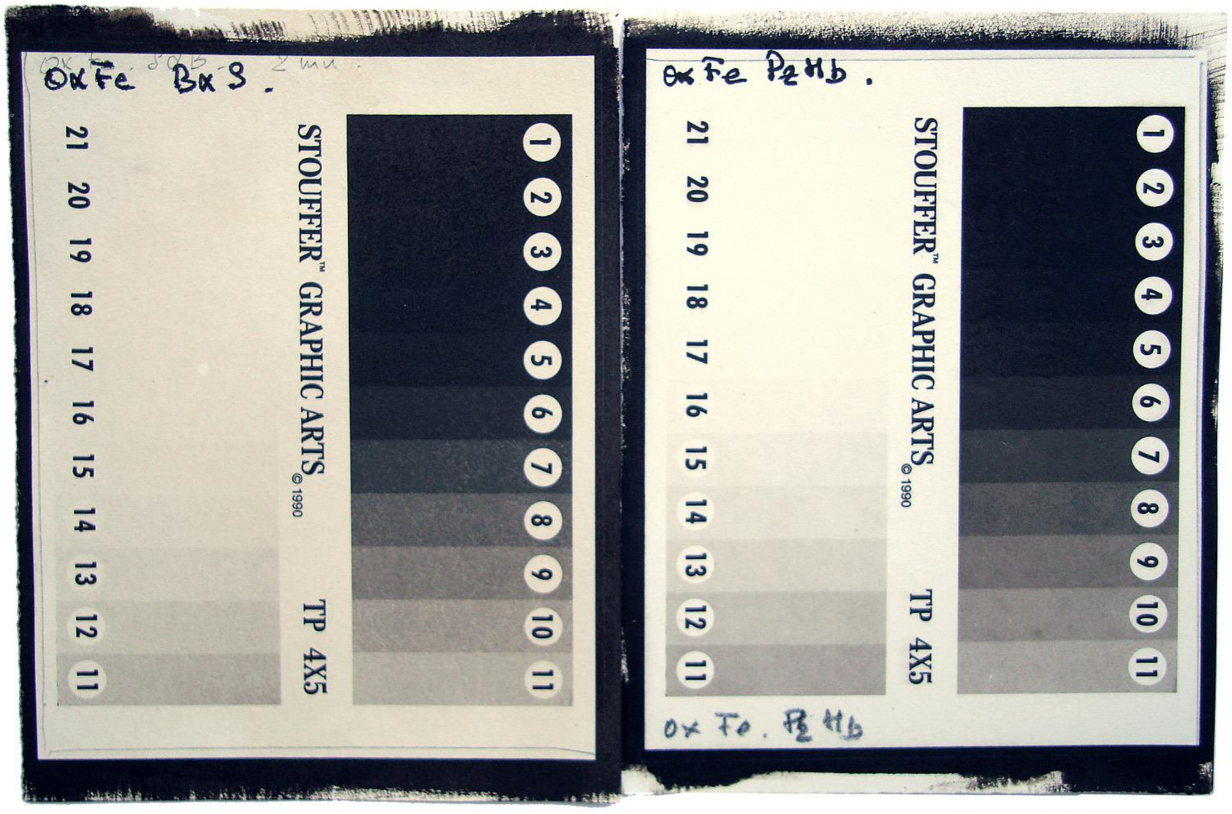
The oxalate obtained during this experiment has got a 27 % concentration, and the aerometer indicates 1.17. A 24 % concentration is suitable too with no real differences in what the picture looks like.

Another way of proceeding consists in weighing the same volume of water and the same volume of ferric oxalate, the ratio between both results has to be 1.174.

Once the filtering stage is over, add some oxalic acid, 2 grs for 100 cc of water. You can heat the mixture in a bain-marie up to

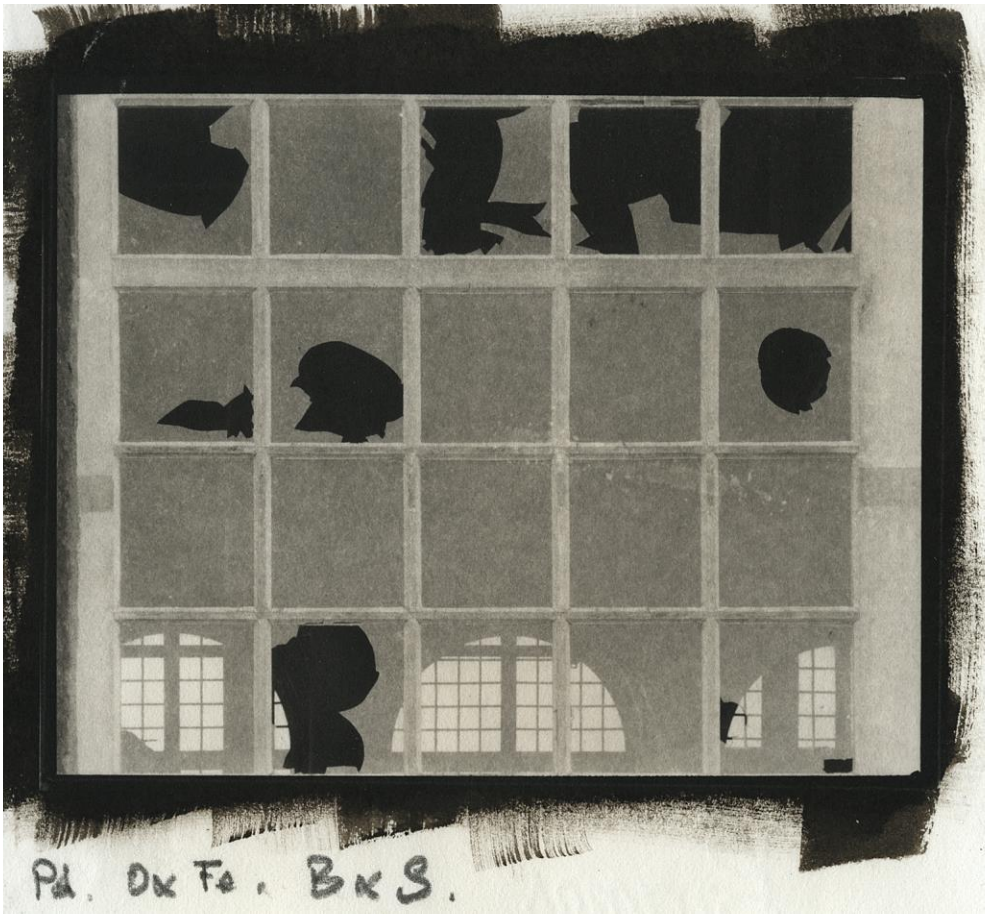
30°C, not more, for it to liquefy more easily. Note that this is very important as it stops the veil from developing too much.

♦ Report on the test-printing of a negative, with a Stouffer step tablet



Comparison between both prints realized with the same Stouffer Chart, one with B&S (Bostick and Sullivan) ferric oxalate, the other one with Pz&Hb ferric oxalate

. The Pz&Hb formula (Pizzighelli and Hübl) and the B&S (Bostick and Sullivan) formula show a similar gradation, but their Dmax is very different: a 2.28 Dmax for Pz&Hb against a 1.55 Dmax for B&S. (Measures taken by transmission in the densitometer). On the other hand the rendering is grainier with the B&S formula with a veil which tends to appear and which makes clearing more difficult.



With B&S ferric oxalate

With Pz&Hb ferric oxalate

♦ Report on the test-printing of a negative

We find the same differences. The density of the darkest part of the print (the small upper right-hand side black circle) is 2.08 for the print with Pz*Hb OxFe and 1.56 for the print with B&S OxFe. The gradation is nearly the same, but we find a grainy structure again on the print with B&S OxFe, whereas the smooth areas are quite uniform on the print with Pz&Hb OxFe.

The conclusion that we can draw from these tests is obvious. Or as we say in French: " il n’y a pas photo ".

♦ preservation

The Pz&Hb ferric oxalate ensures a good preservation, but bacteria can develop. To prevent them from developping, add 0.1 % of sodium benzoate.