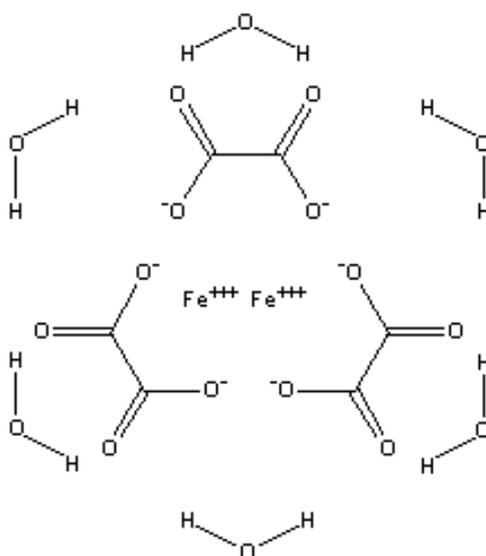


PREPARING
FERRIC OXALATE
POWDER

Ferric oxalate hexahydrate



(CAS number: 19469-07-9)



[19469-07-9.gif]

(by Vicente-M. Vizcay Castro, August/1999)
(English revision and adaptation by Jeffrey D. Mathias)

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INTRODUCTION

The procedure of preparing ferric oxalate powder is believed to be of great interest to alt-photo community. We consider that knowledge must be shared, not hidden, not used to one's own advantage or in one's own interest.

Ferric oxalate (CAS number: 19469-07-9) is a sensitizer for some of the iron based photographic processes. The dry powder form is desired because of its superior storage characteristics. It is therefore an advantage for one using such a material to be able to make it themselves from readily available materials and commonly available low-cost equipment. Taking as reference the 1999 prices of Alfa-Aesar for the reagents (grade ACS and 1000g size), a derived price for the ferric oxalate of about \$0.13/g. (only considering the reagents, no other cost considered).

The "modus operandi" has been adapted so as not to require specific laboratory equipment and to allow for the use of low-cost elements. Efforts have been made to illustrate and to maximize the details of the evolution of the reaction and the subsequent processes. The most tedious phases are those with the purpose of removing the water and nitric acid from the precipitate.

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THE PROCESS REACTION



	<i>FeNi</i>	<i>OxAc</i>	<i>FeOx</i>	<i>NiAa</i>	<i>Wa</i>
Fw:	403.99734	126.06604	483.84048	63.01288	18.01528
Eq:	807.9947	378.1981	483.8405	378.0773	324.2750
Grams:	250	120	149.70	116.98	100.33

Note: *Only for WordPerfect format:* If you introduce (where there is 250) a value (grams of ferric nitrate), these table give you the necessary amount (in grams) of oxalic acid necessary to react with the nitrate and the amounts (in grams) of the other products obtained. The theoretical amount of oxalic acid has been increased in a 2.5% to achieve that all ferric nitrate react.

REAGENTS:

The quality of the ferric oxalate obtained depends on the quality on the reagents (ferric nitrate and oxalic acid) used.

Ferric nitrate nonahydrate: $(\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O})$. Pale-rose-violet deliquescent small crystals. Turns brown in air contact.

Dangers: Fire risk. Dangers in contact with organic materials. Strong oxidizer. Irritant.

Oxalic acid dihydrate: $(\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O})$. Transparent acicular small crystals.

Dangers: Toxic by inhalation and ingestion. Irritant.

PRODUCTS:

Ferric oxalate hexahydrate: $(\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O})$. Amorphous powder pale-yellow.

Dangers: Flammable. Corrosive. Toxic by ingestion and inhalation.

Nitric acid: (HNO_3) . Diluted in the reaction water. The resulting liquid of the reaction has a concentration of the 40-50% of nitric acid.

Dangers: Toxic by inhalation. Erodes the skin and the mucous membranes. Corrosive. Strong oxidizing agent.

Water: (H_2O) .

All chemicals involved in procedure are common in alt-photo processes, with the exception of nitric acid (40-50% concentration). Take care and consult : MSDS (*Material Safety Data Sheets*), RTECS (*Registry of Toxic Effects of Chemical Substance*), LCSS (*Lab Chemical Safety Summaries*) and "*Prudent Practices in the Laboratory: Handling and Disposal of Chemicals.*" by National Academy of Sciences.

As a consequence of the compounds involved in this reaction and during all the phases of this process, it is recommended that the following are employed:

- S well-ventilated work place.
- S protective gloves, preferably nitrile or polypropylene.
- S safety goggles or glasses.
- S activated charcoal respirator or mask.
- S rubber or polypropylene apron, lab coat or old clothes
- S labware of Pyrex glass or similar, polypropylene, etc.
- S stainless steel or plastic implements (spatulas, spoons and knife).
- S plastic bucket for neutralizing waste

PROCEDURE

Remember to neutralize used utensils and waste liquids and papers prior to disposal.

WEIGHING:

The following amounts of reactants, with this procedure, should produce 125-149 grams of ferric oxalate dry powder. Proceed as follows:

- 1: In a "high sided" precipitates beaker of 500 ml. weigh 250 grams (g.) of ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$). Break up any lumps that exist.
- 2: On a paper weigh 120 g. of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$). Preferably in powder or small crystals form.
- 3: Distribute the oxalic acid into 3 or 5 portions of approximately equivalent size, each one on a different paper.



[Step3.jpg]

MIXING AND REACTING:

From this point, the process must be carried out in a well-ventilated area and with safe light (normal ambient light may be OK). Avoid direct sunlight, high intensity light or fluorescent light.

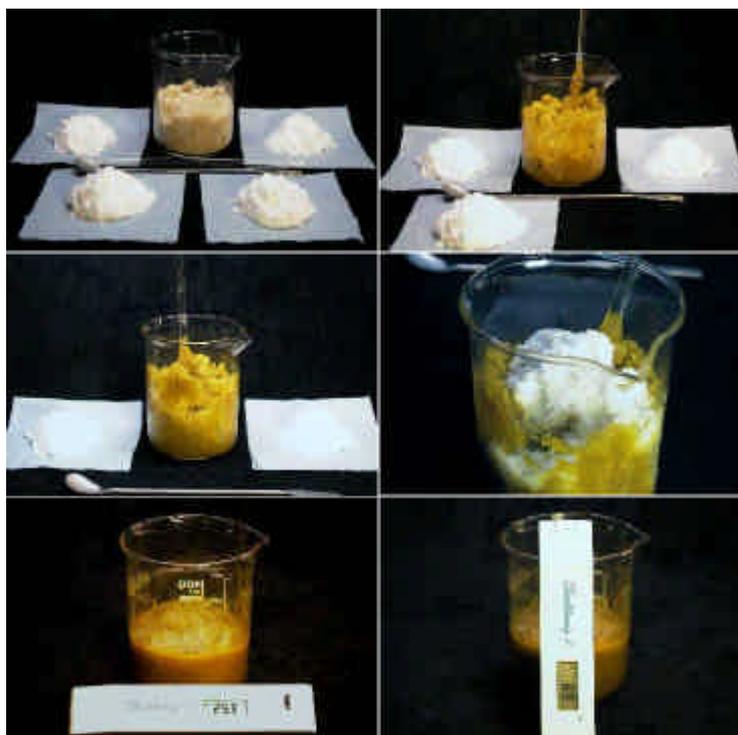
4: The following procedure is designed to mix, as uniformly as possible, the oxalic acid and the ferric nitrate. To do this:

- a) Take one of the portions established in step 3 and pour it in the beaker that contains the ferric nitrate.
- b) With a strong glass or plastic rod stir for 1 or 2 minutes.

This will mix the oxalic acid and the ferric nitrate more uniformly in the beaker. The reaction (endothermic, the beaker cools) begins at the moment of contact between the oxalic acid and the ferric nitrate. In the contact zones, between both reactants, colors appear that change from green to yellow (ferric oxalate). Since the reaction produces water, the mixture is humidified and liquefied during the process which in turn facilitates the mixing process.

- c) Repeat a) and b) until all the oxalic acid established in step 3 has been mixed with the ferric nitrate in the beaker.

At the completion of this step, the temperature of the mixture can go down to 8-9 °C (for an ambient room temperature of 25-28 °C)



[Step4.jpg]

5: Cover the beaker with a piece of plastic kitchen film and let it rest.

To help homogenize the reactants and products, during the next 2 or 3 hours and each half an hour, stir the contents of the beaker with the rod. This has to be done gently to avoid splashes, since the content of the beaker already contains nitric acid. Take care to always replace the cover with a new piece of plastic film.



[Step5-cover.jpg]

If mixture is uniform the following is observed:

15 minutes after step 4 was ended (S4E), the mixture has been liquefied enough, displaying a yellowish brown green coloration. The mixture is quite fluid with bubbles (air), easily moves when inclining the beaker, and has a temperature of 8,5°C. The part of the beaker's wall over the mixture, appears partially covered with dry yellow particles of FO.

30 minutes after S4E, the green tonality of the mixture has disappeared and has become a yellowish brown color.

60 minutes after S4E, the ferric oxalate begins to precipitate (slowly). The mixture color is very similar to coffee with very little milk. The mixture temperature has risen to 11 °C.

It is observed throughout next the 2-3 hours, that the coffee color disperses (as if adding milk to coffee drop by drop).

150 minutes after S4E, the color is pale-yellow, somewhat brown. The mixture temperature is 13°C.

180 minutes after S4E, the color is more yellowish than above. The mixture temperature is 14°C.

If mixture isn't uniform the following is observed:

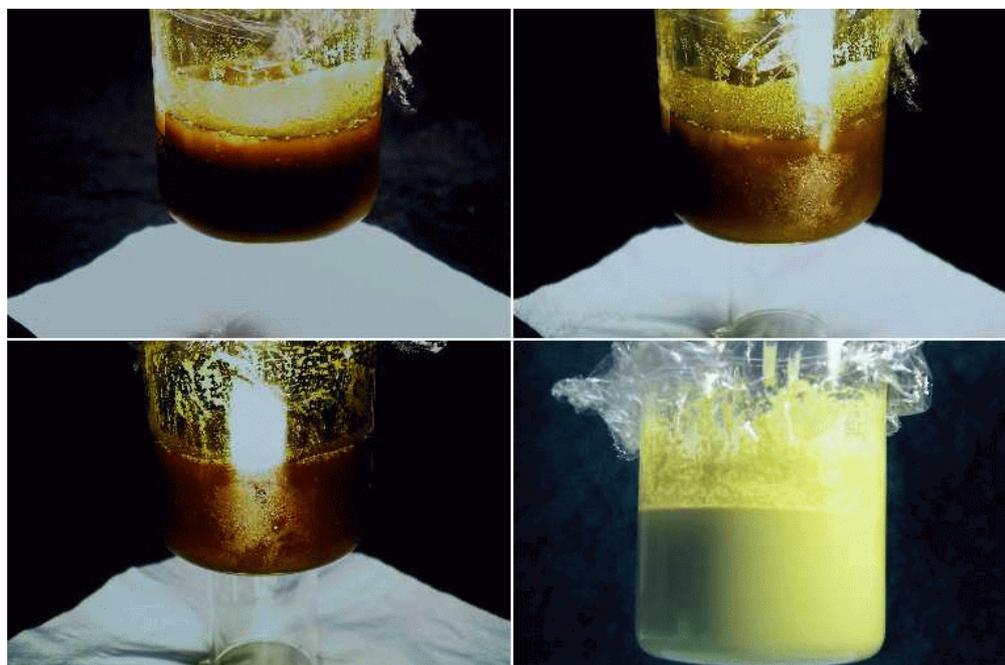
The mixture displays a yellowish coloration in the lower part and brown-yellowish in the upper part. At the bottom of the beaker some zones appears that are opened in fan-form of a yellow-greenish color. This type of structure is a consequence of the fact that the reaction speed is not homogeneous due to the heterogeneous nature of the mixture (the reactants and products concentrations are different at various points of the mixture). The occurrence of the yellow color indicates that, in the points where this color appears, the concentration gradient of ferric oxalate is so high that it supercedes the solubility product of the oxalate and precipitates.

During this step two layers are observed, one more fluid and light (superior) and the other more compact and granular or earthy texture (inferior).

It is observed that the beaker externally presents a strong condensation motivated by the low temperature of the beaker.

At an ambient temperature of 24-28°C the beaker temperature can go down to 8-12°C.

After these 3 hours, observe that the content of the beaker, when stirred, is a yellow mixture of earthy texture due to the initial reactants that didn't react. The external condensation may continue.



[Step5-resto.jpg]

- 6: After 6-8 hours, since the initial mixing process was ended (step 4), observe that the contents of the beaker is of a pale yellow color and has curdled. That is to say, it resembles cement and is solid so that it does not fall out of the beaker when inverted and presents resistance to the penetration of the glass rod. With care (applying gentle force to avoid that the beaker will be broken), penetrate this mass with the glass rod in several points and observe that it is liquefied. Repeat several times in order to liquefy the contents of the beaker as much as possible. Once liquefied, try to dissociate with the rod or spatula, the lumps that exist in order to obtain the most homogeneous fluid that is possible. Stir with the glass rod until the content acquires the appearance of smoothly beaten yogurt or yellow-greenish cream.



[Step6.jpg]

The mixture is a finely divided precipitate of micro crystals which tends to be colloidal and to aggregate with itself, and as a consequence can be separated by decantation (rest). The color it becomes is dependent on the size of the groupings: small (pale-yellow-greenish) or large (pale-green). The size of the groupings is dependent on the temperature which the reaction is carried out ($>$ temperature = $>$ size).

The reaction can be considered finished when the temperature of the contents of the beaker is equal to the room temperature.

DECANTING:

- 7: Since the product obtained will be a fine powder (particle size of 5-15 microns), indicative of small groupings of particles, let the beaker rest, covered by the plastic film, during 1-2-3-4..... days (the longer, the better) in order to achieve a certain separation by gravity.

The separation process by normal gravity (not forced sedimentation) is very slow, due to the small size of the groupings of particles. An approximated estimation of the settling (sedimentation) time can be calculated. First establish the following hypothesis:

- Solid density = 2,5 g/ml
- Liquid density = 1 g/ml
- Solid particle size = $10^{(-5)}$ m
- Temperature = 20°C
- Dynamic viscosity = $10^{(-2)}$ g/cm/s
- Acceleration due to gravity = 980 cm/s²

then obtain:

- Terminal settling Stokes velocity:

$$v = 8,17 \times 10^{(-7)} \text{ cm/s}$$

- Time for settling (for 8,17 cm):

$$t = 340 \text{ hours.}$$

These results are for an isolated particle. The interactions between particles, the density of the fluid and the real dynamic viscosity (variables in the time) might cause the time to be multiplied by 100 or 1000.

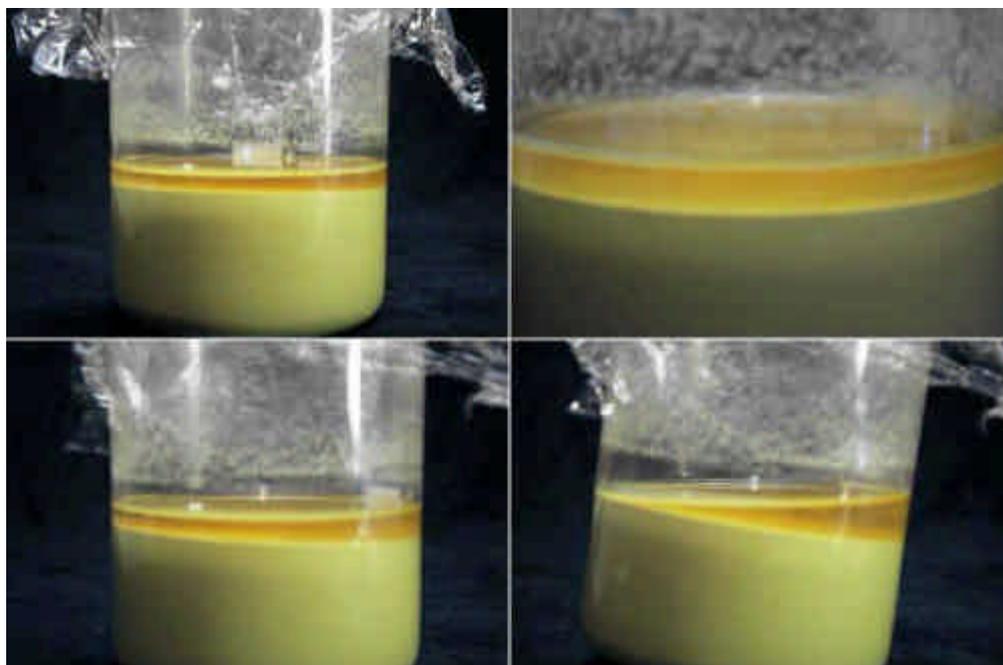
The sedimentation speed can increase by:

- S increasing acceleration (*centrifugation*).
- S increasing of the solid particle size (*adding 0,5g of aluminum sulphate (it reduces the repulsion forces between particles facilitating flocculation), with further mixing to homogenize its distribution in the mixture*).
- S increasing of the solid particle size and temperature, and reducing liquid density and dynamic viscosity (*by heating the suspension, this causes it to coagulate and facilitates separating the precipitate from the solution (temperature at least 40°C but not >50°C)*).

- 8: Every day change the plastic film since it becomes etched by the nitric acid. Observe that floating on the yellow phase appears a liquid phase, almost colorless, that will increase with time. It will reach a thickness of several millimeters (it depends of ferric nitrate humidity), which represents something less than 10-15% of the H_2O and HNO_3 formed in the reaction).

Increasing the days that it rests will facilitate the deposit compaction of the suspension making easier to eliminate the liquid by pouring off (this liquid has a nitric acid concentration of 40-50%).

- 9: The liquid that floats above the yellow precipitate (ferric oxalate) should be withdrawn as thoroughly as possible and **neutralized**.



[Step9.jpg]

DRYING PHASE I:

The purpose of this phase is to remove the maximum amount of acid and water mixture from the precipitate. This is achieved by capillary action by application of absorbent paper (this paper can be: napkins, white kitchen paper towels, etc) .

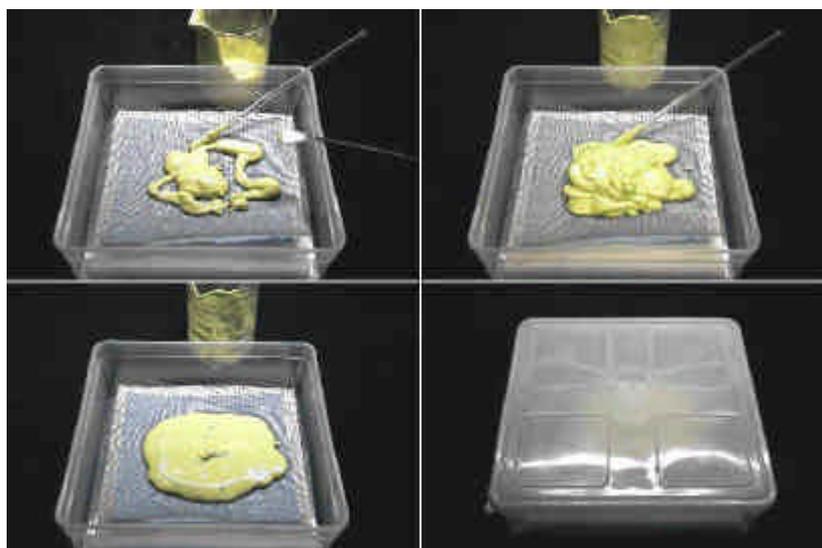
ATTENTION: the following steps should be carried out with wearing gloves (always), goggles , mask and in a well-ventilated place with normal illumination (as in step 4). Drying is considered to be eliminating, as thoroughly as possible, a nitric acid solution with a concentration of the order of 40-50%, that impregnates the ferric oxalate. Avoid more than 3-4 hours of contact of the oxalate with the absorbent papers since these are etched by nitric acid and become fragile.

- 10: Prepare a plastic container (at least 30x30 cm square) with a hermetic cover, such as those which are used to preserve nutritional products in a refrigerator (Tupperware, Rubbermaid, Curve, etc) by lining its bottom with 10 or 20 absorbent papers, over these papers place a piece of 25x25 cm plastic or glass fiber mesh, e.g. mosquito netting or fiberglass screen.



[Step10.jpg]

- 11: Liquefy the contents of the beaker (as described in step 6). With the aid of plastic or stainless steel spoons, spatulas or knives, the precipitate is removed by loosening it, little by little, and placing it onto the mesh and spreading it, leaving an edge of 1,5-2 cm free. Next, cover the container with its lid.



[Step11.jpg]

- 12: After 3-4 hours open the container and observe where moisture has penetrated the papers.
- a) Remove the moist papers and replace with new ones.
 - b) The consistency of the precipitate at this time will be quite firm. Place 3 or 4 papers on top of the mass and strike on top with the fist several times (this is to seat and loosen the mass and at the same time to extract more liquid from the upper part of the mass)
 - c) Repeat a) and b), at intervals of several hours (2-3h), until it is observed that the moisture that impregnates the papers is insignificant, indicating that this phase of drying has ended.

Dispose of papers by diluting in a bucket of water and neutralizing to pH 7, then pouring liquid down the drain with water and placing fully neutralized papers with other trash.

DRYING PHASE II:

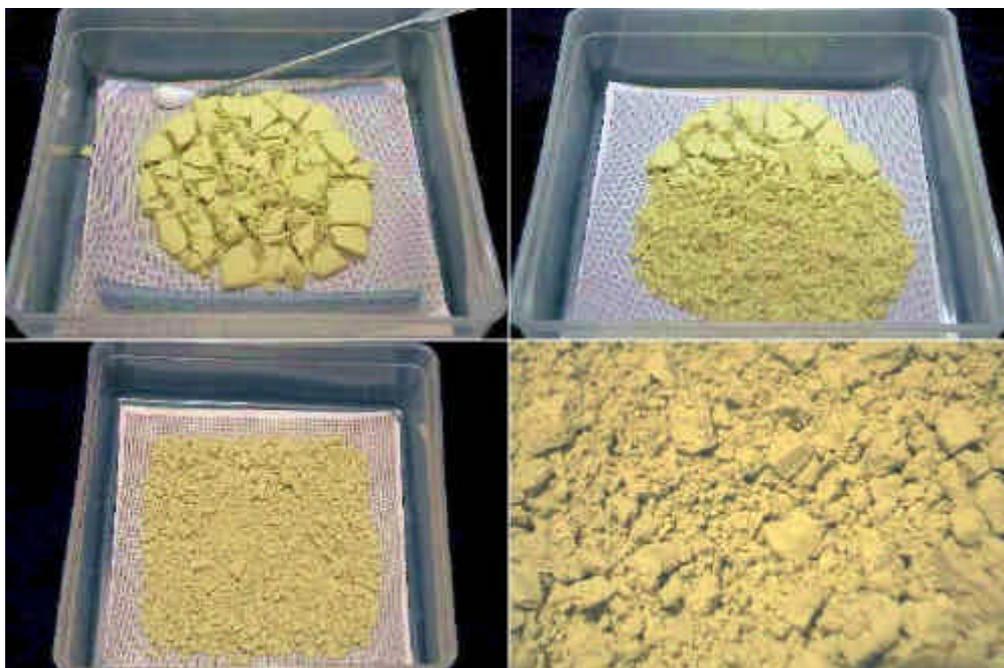
- 13: Move the precipitate along with the mesh onto new absorbent papers (5 or 10 layers) which are placed into the container (the mesh can be removed after the third or fourth change which will be made in this phase, leaving the precipitate directly on the absorbent papers).

The container should be left open to facilitate the drying and elimination of the nitric acid and water. The container should be located in a place without light which is well ventilated. The air can be forced to circulate over the container as a soft current (that does not blow away the oxalate powder).

Take into account that the gases eliminated in the process of drying are very corrosive and strong oxidizers. Any iron or steel present will be oxidized.

With the spatula or knife, break up, as much as practical, the precipitate chunks that have been deposited on the absorbent paper. Spread it uniformly over the mesh-paper.

With each paper change, reduce the size of the chunks with the aid of a spatula or knife.



[Step13.jpg]

- 14: Repeat step 13, 5-8 times each 2 or 3 hours. When nearly all that is on the paper is a pale-yellow powder and small chunks, this phase can be considered as ended.



[Step14.jpg]

Dispose of papers by diluting in a bucket of water and neutralizing to pH 7, then pouring liquid down the drain with water and placing fully neutralized papers with other trash.

DRYING PHASE III:

To dry further, the ferric oxalate is moved to a plastic or glass container with hermetical cover (which will have conditioned so that these can contain a drying agent (dry calcium oxide or hydroxide, zinc oxide, etc) which is not in direct contact with the oxalate).

Keep the oxalate in the container until it is considered sufficiently dry, then move it to the final container, an amber glass bottle with hermetical cap.



[Dry-Ph III.jpg]

OPTIONS:

- ! Steps 4 to 9 can be accelerated by using a magnetic stirrer. If the stirrer is a hotplate stirrer, it is possible to heat and stir the mix (temperature not $>50^{\circ}\text{C}$).
- ! If one is impatient they can skip the decanting steps and directly go from end of step 6 to DRYING PHASE I.
- ! Some of the drying steps can be obviated or simplified if the liquefied precipitate obtained at end of step 6 is submitted to filtration (vacuum filtration better). For this use filters type Watman 50 or Millipore 4.

CONCLUSION:

The theoretical weight of the ferric oxalate obtained in this reaction is about 149.7grams. There are losses as a consequence of the numerous raking of the oxalate, as well as the portion dissolved in the eliminated liquid. With care, somewhat more than 125 g of dry ferric oxalate is obtainable.

The obtained ferric oxalate contains some residual oxalic acid and nitric acid, witch prevents ferric oxalate reduction with time.