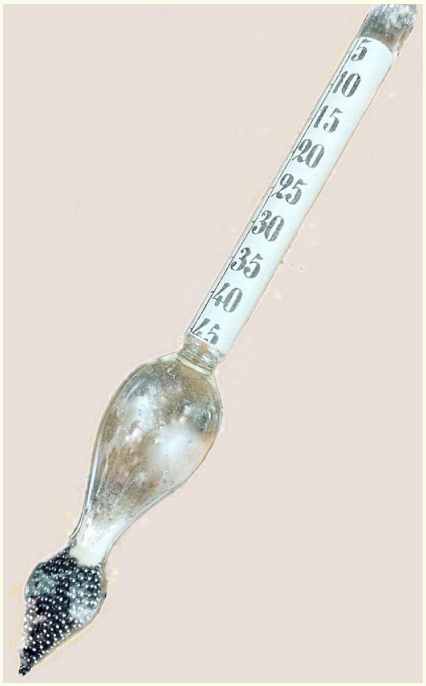
APPENDIXES for heliogravure

(as mentioned in previous sheets)

APPENDIX 1 - Concentration and acidity control.



The control of $FeCl_3$ concentration is carried out by means of an appropriate *densimeter* in the required scale range: generally 30÷50 °Bè. The measurement is elementary since the instrument consists simply of a ballast of small weights placed in the lower part and a graduated scale in the upper part, all sealed in a glass tube. The instrument is plunged in a fraction of the liquid - free of foam and air bubbles, at the correct temperature usually indicated on the scale of the instrument itself – to fill a graduated cylinder. When the tool stops moving, the density value is read off. With this value, any necessary corrections are made to the solution: addition of small amounts of water to reduce the density or of stock ferric solution at higher density to increase it.

As mentioned, the coefficient of T°= 1°Bè/3°C while that of dilution 1°Bè/40 cc/lt

The density measurement (equivalent to $FeCl_3$ concentration) is carried out before each etching session.

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APPENDIX 2 - Free acid neutralisation.

Ferric chloride is not an acid in the strict sense, but a 'salt' with very pronounced acidic properties, but without production of gases or vapours during the corrosive reaction. In its solutions, the dissociation of the ferric salt produces a certain concentration of chloride ions Cl^- (which increases with time), creating a "free" acidity with uncontrollable effects on copper. This is the cause of the so-called '*devils*', which correspond to violent punctures into the gelatine in the shadows areas of the image (where the layer is thinner), which then resemble small '*lightning bolts*' on the plate when is etched. These will then become visibles in print because of their considerable depth and dimension in relation to the outline, which hold a lot of ink, requiring extreme care when cleaning the plate.
In short, this free acidity has to be counteracted by using ammonia (a weak base) and a small amount of iron salt solution, as said below.

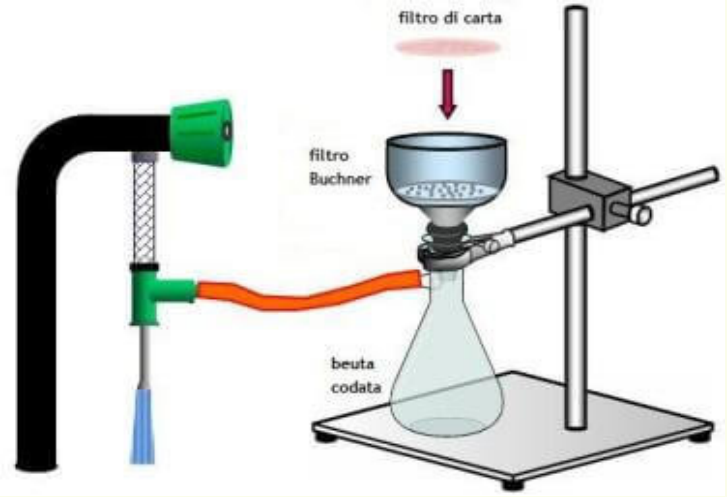
To neutralise about 4 litres of bath (e.g. 1 litre for each of the etching baths), about 50 cc of roughly 37-38 °Bè $FeCl_3$ is placed in a 500 ml beaker.
Add then little by little about 300 ÷ 500 cc of ammonia ≈ 5% (available in supermarkets, for domestic use) while stirring. A gradual thickening of the solution is produced by the formation of a copious precipitate of ferric hydrate, so that may be necessary to continue stirring manually with a glass rod. Once these quantities have been reached, check the pH frequently with a litmus paper until neutralisation by adding small quantities of NH_3 in excess (the reaction is slightly exothermic, work under a fume hood, do not inhale the ammonia or into the reaction beaker!)
This thickened solution of $Fe(OH)_3$, a weak ferric base, is the product that will neutralise the

excess hydrochloric acid in the bath without introducing foreign ions, since the base is composed of Fe^{3+} (i.e. the same cation as perchloride).
But that's not all! In fact, this *slimy* mass cannot be set into our etching solutions until the excess of ammonia has been removed. ...
To do this and not to miss another hurdle, one must equip oneself with (in laboratory products retailers)

- *vacuum flask (preferably fitted with a tap for venting) and rubber conical rings for the mouthpiece,*
- *small length of vacuum tube,*
- *500 cc at least Buchner funnel,*
- *white band filters (with diameter equal to the bottom of the Buchner)*
- *small vacuum pump (which can be water-powered like the one shown, connected to the water tap, or electric).*

The apparatus makes it possible to produce a discrete vacuum in the flask, so filtering the liquid and retaining the ferric hydroxide on the funnel filter (image from: *https://www.chimica-online.it/download/filtro-buchner.htm* - the supports give greater security during execution).

The mass thus obtained by precipitation with ammonia is carefully "diluted" in a few tens of cc of water, poured little by little into the funnel, the floor of which is covered by the paper filter, start the vacuum (open the tap!) and go. When the filtration slows down, the filter with the accumulated mass is carefully removed and set in a beaker and a new filter is placed in the funnel. At the end of filtration — which is neither painless nor very fast; remember to wear gloves and face protection — collect as much of the precipitate as possible from the filters, while discarding the liquid in the flask, consisting of water and NH_3. Add more water, dilute, etc.



After at least two filtrations, check for the presence of ammonia, roughly with the nose on the mass itself —now almost odourless — or more politely with a litmus paper on the last liquid poured into the flask. Only if you are not close to neutrality make another filtering session. The precipitate has to be used 'fresh', within a week of preparation.
Portions of it is now scattered (the preparation turns out to be rather *stuck*) in each of the baths to neutralise, either in the bottle or, better still, in the basin, and left overnight in its capped vessel before the bath is considered 'neutral' for meeting the copper plate.

N.B.: From personal experience, these operations should be repeated every 3-4 weeks, or if you do not perform an etching for more than a month, to be on the safe side. There is no direct measurement of the presence of free acid alone in this case.

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APPENDIX 3 - Table of densities of $FeCl_3$

The chart gives the density in degrees Baumé, plus the specific gravity and the percentage by weight of anhydrous salt and the grams of salt per litre, measured in a solution at 20 °C.

DENSITÀ DI SOLUZIONI ACQUOSE

TABELLA CXLIII – Cloruro ferrico a 20/4 °C.

BÉ	P. SP.	$FeCl_3$ % in peso	g/litro	BÉ	P. SP.	$FeCl_3$ % in peso	g/litro
1,0	1,007	1	10,07	20,2	1,162	18	209,2
2,1	1,015	2	20,30	22,3	1,182	20	236,4
4,5	1,032	4	41,28	27,5	1,234	25	308,5
6,8	1,049	6	62,94	32,7	1,291	30	387,3
9,1	1,067	8	85,36	37,8	1,353	35	473,6
11,4	1,085	10	108,5	42,7	1,418	40	567,2
13,7	1,104	12	132,5	47,4	1,485	45	668,3
15,9	1,123	14	157,2	51,5	1,551	50	775,5
18,0	1,142	16	182,7				