THE IRON-SILVER PROCESSES

Photo: Dante Cappellani - print: Stanze di Luce

A compilation of notes from various Picto Benelux members,
and main articles published about these processes
in the specialised litterature.

Jacques Kevers - 2014

I - Let's not confuse...

The main processes being part of the iron-silver family are the Kallitype, Van Dyke Brown, and Argyrotype.

And no: Calotype is not part of them. It even doesn't have anything to do with them! Calotypes were designed by Henry Fox-Talbot from his "Photogenic Drawings" and are based on the transformation of silver nitrate by sodium chloride (salt) into silver chloride. Calotypes are essentially negatives – at first, as their low sensitivity required very long exposure times, their use was restricted to photograms; later improvements made it possible to use them also directly in cameras. With them, Fox-Talbot threw the bases of the negative-positive system which was used until the advent of digital photography. It has to be noted that for positive documents using the same technique, we do not call them any more calotypes, but salted paper prints, or salt prints.
These processes, based on the photosensitivity of silver salts alone, are not the object of the present document. Those who would like to know more about them should read "Salted Paper: History and Practice" drafted by Lionel Turban, edited and translated by Picto Benelux, downloadable here: http://www.picto.info/saltdoc/papsal_e.pdf.

Here , we only will deal with the processes based on the reduction of iron salts by light. They divide into three big families: the cyanotypes, the processes based on noble metals such as platinum, palladium and gold, and finally the "iron-silver" family, where silver salts lying in contact with ferrous salts are turned to the metallic state. The last-named family is the specific subject of this document.

Even within this family, confusions are not rare. It often happens that people believe they are making Kallitypes, while in fact they are using the Van Dyke process – a little more recent and simpler – and conversely. In fact, the term "Kallitype" gradually became kind of a generic name for the "iron-silver" family.
As for the Argyrotype, this is a much more recent technique, developed by the British Michael Ware, where silver nitrate is replaced by silver sulphamate in the sensitizer. The big advantage of this process is that an acid solution can be used, which makes the clearing much easier. Other processes use neutral or basal solutions producing iron hydroxide (rust..) which can be difficult to eliminate and affect the highlights of the image.
With Kallitypes, ferric oxalate is used to sensitize the paper; during the exposure, only a very faint image will appear, that has to be processed to appear completely. Depending on the choice of papers & developers, various tints can be obtained: sepia, red, eggplant and even blacks very close to those of platinum-palladium prints.
All things considered, Kallitypes appear in fact to be closer to the platinum-palladium process, whereas Van Dyke Brown (VDB) stays closer to the Cyanotype process: for VDB, sensitization is also based on ferric ammonium citrate, and the image is asking only for a wash after exposure to appear completely.

When speaking about Kallitypes in this document, we only refer to the original process, slightly more complex and more expensive, but offering more flexibility for contrast controll than VDB.

II - A little bit of history...

As of 1842, Sir John Herschel (1792-1871) discovered that light could transform the ferric ammonium citrate in a ferrous state, and that permanent images could be formed by the reduction of a noble salt into metal there where it was in contact with the ferrous salts . He used prussian blue pigment, mercury, gold and silver, to describe processes which he called respectively: cyanotype, amphitype, chrysotype and argentotype. Absorbed by his other multiple activities, he never pushed much further his investigations, and it took a long time before others actually implemented processes derived from his argentotype.

Only in 1889, Dr . W.W.J. Nicol developed and patented the Kallitype process and its variants, which he called without a lot of originality Kallitype I, II, and III. These variants used salts such as ferric sodium citrate, potassium oxalate, ferric oxalate, oxalic acid, as well as various developers.

In 1895, the company "Fabrik Technischer Papiere Arndt und Troost" from Frankfurt patented a process called "Braundruckverfahren" (brownprint) producing sepia prints. This patent describes a mixture of ferric ammonium citrate, silver nitrate, tartaric acid and gelatin. This formula did undergo numerous changes, and eventually the gelatin disappeared since the modern papers ended up being well sized at production stage.

It has to be pointed out that the "Van Dyke Brown" name only appeared much later, towards the end of the 1930s - the beginning of the 1940s. The origin of this name is not known for sure: some people think that it refers to the palette of warm colors used by the Flemish painter Antoon Van Dyck. Anyway, the name is in fact wrongly used for the process considered here: the "Vandyke" process mentioned in the early 20th centuries' literature referred to a photo-lithographic process used for the making of topographic maps. It was developed by Frederick Reginald Vandyke who was hired by "Survey of India" (a cartography institution) in 1889, and ended his career as director of the Photo-Litho Service company in 1923.

The "Van Dyke Brown" name became however gradually of common use, and the term was defined for the first time as a photographic technique based on an iron-silver salts combination in the Encyclopaedia Britannica of 1961.

III - Technical descriptions

A - The brownprint

This certainly is the least known/used process in the silver-iron family.

a - The "Arndt und Troost" formula

ferric ammonium citrate	*100gr*
silver nitrate	*20gr*
tartaric acid	*20gr*
gelatin	*15gr*
water	*1000ml*

b- "Contemporary" version

The sensitizer is similar to the one used for VDB , but resorts to the use of tartaric acid instead of oxalic acid.
To sensitize the paper:

demineralized water(*)	*30 ml*
ferric ammonium citrate	*2,5gr*
oxalic acid	*0,4gr*
silver nitrate	*1,0gr*

Dissolve and mix at first the citrate and the oxalic acid, then add the dissolved nitrate under subdued light. It is possible that a sediment forms; this can be filtered out. Leave aside in the dark for 24-48 hours. If this formula does not give enough contrast, it can be increased either by sizing the paper with gelatin, or by adding to the formula a drop of a 10% potassium dichromate solution. In this case, there might be again a precipitate, that has also to be filtered out.

Exposure: sun or UV. Expose as for a Kallitype or a VDB. Only faint traces will be visible before processing, as it is the case with Kallitypes.

Processing:

DM-water:	*1000ml*
borax	*5gr*

Immerse the print for 5 to 7 minutes in this bath, with constant agitation.
Borax (instead of straight water for the Van Dyke) is used for the processing; it is quite alkaline and favors the formation of iron hydroxide, which is very difficult to eliminate. The problem can be reduced by immersing at first the print in a bath of salted water, slightly acidified with a pinch of citric acid.

Fixing: 1 minute in a 3% solution of sodium thiosulphate. Overall, the image will darken, but the highlights will clear.

Rinse: After a first bath (5 min.) in a 1% solution of sodium sulphite, rinse in running water for 20 minutes. If no sulphite bath is used, one might have (in case of rather hard water) to acidify the water with a pinch of citric acid and to extend the rinse for 40 minutes.

(*) *Truly distilled water is expensive and difficult to get; and anyway, it will still contain chlorides (Cl-) responsible for the formation of the opaque white AgCl precipitate when in contact with silver nitrate. For our needs, a good quality (≤ 1µs) demineralized (also called DM or deionized) water does contain neither chlorine, nor chloride, and is more than adequate.*

B - The Kallitype Process

The Kallitype process never was quite popular. It got some positive assessments - especially in the United States - but had the bad luck to arrive 10 years after the platinum process with its enormous prestige, and just before the very popular "gaslight" paper. Neither quite as permanent as the first one, nor as user friendly as the second one, it got a reputation of instability which was especially detrimental.
This reputation was mostly due to clumsy processing, in particular to bad fixing: Nicol in his first formulae used ammonia only to fix the image. Things improved when this was replaced, totally or partially, by sodium thiosulphate. Permanence depends indeed largely on the complete elimination of the iron salts with an appropriate solvent, and of the unexposed silver salts with thiosulphate. It can be further improved with various toners.
Over time, Nicol's original formulae were strongly modified. They therefore have only some historic interest, and we will not delve further into them here.

The Kallitype is a developing out process (DOP), which does not have the automatic masking effect of printing out processes (POP) nor the related reduction of contrast in the shadows. Its curve presents a long and regular slope, similar to that of the platinum process. A good Kallitype is very difficult to differentiate from a pt/pd print – but much cheaper...

Workflow: Sensitizing – drying – exposure – development – washing/clearing – toning (optional) – fixing – wash.

Sensitizing bath: While Nicol's original formulae brought in a number of products, with in particular of ammonium oxalate and oxalic acid, the contemporary formula is much simpler and contains only 2 substances. Prepare two solutions (in subdued light for the silver nitrate):

A - a 10% silver nitrate solution
B - a 20% ferric oxalate solution

Keep them separated, in brown bottles and away from light.
When ready to coat, mix equal parts of A and B (avoid contaminating solutions by dipping a dropper in the other bottle..) for just the quantity you need. Mix with a circular movement (as if you were turning a glass of wine..). A Kallitype requires about 20% more products than a platinum print. As a starting base, foresee (A+B solution): for a 10x12,5cm print: 16-20 drops , for a 13x18cm: 1,5ml (or 34 drops), for a 30x50cm: 6-8ml, and for a 50x60cm: 14ml.
if your prints tend to fade, you can slightly increase the amount of A vs B.
The following might be prepared/used too:

- *1 drop of a 1% gold chloride solution per 20 drops of A+B (warmer tones, olive-black)*
- *1 drop of a 5% Tween20 solution per 20-40 drops of A+B (better absorption in paper)*

Only use Tween20 when really necessary (with Bergger's COT320 for instance.)

Drying: If using a hairdryer, it is important not to blow the hot air directly on the wet surface. This would fog the highlights. Use the low temperature setting and direct the air flow to the back of the paper. Even better, use an air fan instead.
Attention! The paper has to be "bone dry" before use! By wet weather, a simple air drying, even for a prolonged time, might not be sufficient.

Exposure: Proceed as usual, maybe with the help of a "Stouffer" (or similar) step wedge. The exposure will be shorter than for a pt/pd print, and should be around 1-6 minutes in the sun; you might have to double that time under a UV lamp. It all depends from several variables of course: lighting equipment, paper, negative, etc..

Development: quite a lot of different formulae exist, giving all different results (image color,...). Of course, if you intend to tone your image, the effect on image color is of little importance...

The image appearing very quickly when it gets in contact with the developer, it is important that all parts of the print are immersed at the same time. The most common technique is to put down the exposed paper in an empty, clean and dry tray (clean it before each new print) and to pour the developer over it as quickly as possible.

Use enough developer to cover the entire image, otherwise there will be a risk of irregular development and of exhaustion before the processing is complete. Too weak a developer will leave stains on the image. It is advised to add at least 50ml of fresh developer after every 500cm^2 processed. It is also good to keep track of the number of prints processed per batch: each developer has its capacity which it is useful to know.

Even if the image does appear quickly (10-20 seconds), you should not refrain from extending the development: it is impossible to overdevelop, and it is important that a maximum of ferric salts are transformed into ferrous salts. Develop during 8 to 10 minutes. The image will seem far too dark, but will clear up later on.

Be careful that the developer does not become alkaline, as this will foster the transformation of the iron in insoluble salts. The acidity should be checked regularly with pH strips or with a pH meter. As soon as the pH increases, add the same acid as already used in the formula: citric, oxalic or tartaric. It will guarantee a better conservation of the image, and cleaner highlights.

Do not throw away the developer, but keep it for the further processings; you might have to get it filtered: after a while, a dark sediment of metallic residues will form.

"Classic" developer (black-brown tones)

DM water	*1000ml*
borax (anhydrous)	*100gr*
Rochelle salt	*75gr*
tartaric acid	*3gr*

For colder tones, increase the quantity of borax and reduce the Rochelle salt (potassium sodium tartrate) – proceed inversely for warmer tones. Be careful: borax does not dissolve well in cold water: start with 750ml at 30°C.
In fact, this developer is not the easiest to prepare, nor the one giving the cleanest highlights.

The following formulae are often giving more satisfactory results:

Combined developer sodium acetate/ammonium citrate

A - a 20% solution of sodium acetate (200gr in 1000ml water)
B - a 20% solution of ammonium citrate (200gr in 1000ml water)

To use: 1 part A + 1 part B. Renew 400ml per 2500cm^2 processed paper.
Solution A can also be replaced by:

C - 150gr sodium acetate + 1,5gr tartaric acid in 1000ml water.

Solutions A, B and C can also be used separately:
A: brown-black images
B: warm reddish to maroon images, well detailed shadows, fine grain
C: neutral black images, deeper blacks than with A.

There are quite a lot of other developer formulae, far too much to be detailed here.

Clearing

After development it is necessary to remove the yellowish stain, especially perceptible in the highlights. It is also indispensable, for permanence, to remove all unexposed ferric salts. Begin by rinsing the print during 4-5 minutes in demineralized water water added by a hefty pinch of citric acid. Follow by an immersion in two successive 4 % EDTA baths (5 minutes in each, with agitation), until highlights are clean. As ferric salts eliminate, the water gets a yellow color. When the color becomes strong and clearing slows down, eliminate the bath: the second replaces the first one, and a new one replaces the second. If you do not have citric acid or EDTA, a 7-Up ® can help you out... Rinse before passing to the following stage.

Toning (optional)

The toning bath allows to change the final image's color, but more importantly to improve the permanence of the image by plating its silver with a more stable metal. It also helps to reduce the metallic sheen in the shadows, which can be the result of too long a development. All the baths used for pt/pd prints or salted papers can be used. Toning occurs before fixing.
Gold: citric acid 5gr + 1000ml DM water + 5 % solution of gold chloride 5ml.
Immerse 5 minutes, or until the result is to your taste. With usage, its action slows down.
Palladium: sodium acetate 2gr + citric acid 2gr + DM water 400ml + 20 % solution palladium chloride (30 drops). Immerse 5 minutes, or until the result is to your taste.
After toning, rinse the print for 5 minutes in running tap water.

Fixing - Washing

Most of the permanence problems come from inadequate fixing and insufficient washing in water that is too alkaline. It would be a pity to have applied yourself up to this stage, just to compromise everything now..
Fix: if too acid, it will bleach the image; if too alkaline, its action will not be optimal...

sodium thiosulphate (hyposulphite) 50gr
household ammonia 5ml
DM water 1000ml

Fix for 2 minutes - Water rinse for 2 minutes, then immerse 1minute in a 1% sodium sulphite solution - final wash in running tap water for 30 minutes. - hang to dry.

Problem: highlights are stained...

Consider following suggestions:

- *add Tween20 to the sensitizer*
- *use acidified DM water for the first rinse before clearing*
- *use the combined sodium acetate/ammonium citrate developer*
- *process for at least 5 minutes*

Problem: contrast is wrong.

- *Adding potassium dichromate to the developer might increase contrast, but with the risk of staining your highlights, and your developer is changed forever... It might be interesting in that case to keep at hand several sets of developer, each one with a different content of 4% dichromate: 4 - 8 - 16 - 24 - 32 ml/l (the higher the proportion, the higher the contrast).*
- *A colder developer (≥ 20°C) will produce colder tones and more contrast; warmer (30°C), it will provide warmer tones and lower contrast.*

Some usable papers (Kallitype & VDB).

Arches Aquarelle, Bergger COT320, Fabriano Artistico (acidified), Canson Crob'Art, Canson Montval

C - Van Dyke Brown (VDB)

photo: Cezar Popescu

This is a simplified version of the Kallitype process. This formula does not require ferric oxalate and the processing is done in straight water. It is in a way the equivalent of the cyanotype process in the silver salts family. This process however does not have the Kallitype's flexibility for contrast controll.

Its benefits:

- *one single sensitizing bath, easily prepared*
- *processing in straight water*
- *inexpensive*
- *fast; relatively short exposure times*
- *rather long tonal scale; toners similar to those used for silver printing*

Its drawbacks:

Just as the Kallitype process, VDB had from the beginning a bad reputation regarding image permanence. Largely wrongly, as the problems came mostly from inadequate processing instructions, transmitted from generation to generation. Once the formation of iron residues during processing and their interaction with the metallic silver in the image fully understood, as well as the importance of adequate fixing and wash, most of its problems can be addressed. It's a pity that a process, that is basically quite simple while giving such beautiful results, aroused so much distrust...

Workflow: Sensitizing – drying – exposure – wash development – toning (optional) - fixing – final wash.

Sensitizing bath: prepare three solutions A,B,C to be combined :

A	***B***	***C***
Ammonium Iron(III) Citrate ..... 27gr DM water(room t°) 100ml	Tartaric acid ..... 4,5gr DM water(room t°) 100ml	Silver nitrate ..... 12gr DM water(room t°) 100ml

Under subdued light, add B in A while mixing slowly (avoid metallic instruments) and pour the whole into an opaque brown bottle, big enough to contain all three parts. Then add C very slowly, otherwise a milky precipitate will form. If that happens, it might eventually dissolve, possibly after a day or two. If this is not the case, some citric or tartaric acid can be added drop by drop , until the solution clears up. Warming the solution at about 50°C before adding the nitrate might help. Some authors indicate that this bath has to mature a few days before use; all do not agree on this point..

Label clearly. The mixture keeps for approximately one year in the refrigerator. If a black sediment forms, it is unnecessary to filter, just be careful to take off the necessary amount of solution without disturbing the sediment. If you do not get the desired densities any more, it's time to renew your emulsion.

It is also possible to keep parts A, B, and C separately and to use a dropper to prepare just the required quantity at the time of use.

Coating of the emulsion: Use your favorite method, brush or glass rod. Avoid brushes with metallic parts. Avoid loading the brush too much: the resulting paper crinkling and puddles formation would be a source of problems during the processing. Spread the emulsion on the whole surface in one direction before beginning in the other one, otherwise you will have an uneven distribution which will show in the final image. As soon as the emulsion begins to ¨set up¨ (it loses its sheen while observing the surface reflection), it is necessary to stop the brushwork, otherwise streaks will appear. (If not used to this, it might be good to train, with a yellow watercolor for example). When all the product is spread, put the paper aside a few

minutes before using a hairdryer (set to the coldest temperature). Rinse and dry the brush in the meantime, mopping it on some household paper. Avoid leaving it on this paper: it could absorb chlorinated components used to bleach the paper. Last advice: make sure the paper is "bone dry" before coating. If the weather is wet, you might resort to a dehumidifier.

Exposure: VDB is a POP (printing out process): the image must be completely visible after exposure and before "processing" – the latter will mainly clean the image without darkening it enormously. A slight overexposure is preferable to an underexposure. Using a Stouffer (or similar) step wedge to make a series of test strips exposed with 30 second increments may help. Under the sun, the correct exposure usually is in the range of 2 to 6 minutes; a slightly longer exposure will be necessary under UV lamps. Given the large number of variables (products, negative, paper, light source) it is not possible to give more precise indications.

"Wash development": One of the usual problems is that the image, which appeared correctly after exposure, seems to weaken and the dark tones to "bleed" during the processing or even later. That's what made the bad reputation of the process. These problems are not inherent to the process, but are due to inadequate processing.

First wash development: it is important to use demineralized water with a pinch of citric acid added. The presence of chlorine or chloramines in the tap water is the main cause of stained highlights and image fading in the fixer. With the use of DM water, the milky cloud leaving the print will be clearly less important. This cloud is silver chloride formed in reaction to the presence of chloride ions in the tap water. Keep agitating the print in this bath during 2 minutes.

(Acidification: the quantity of acid to be added depends on the characteristics of the water. The water should be acid enough to allow a good elimination of the iron residues, but not too much, in order to avoid a reduction of the silver's Dmax. Begin by 1,25gr/l and increase gradually until 30gr/l, as much as needed. If you can't get deep blacks any more, you went too far. A pH just below 7 is ideal)

Second wash development: fill a tray with tap water and add a pinch of citric acid. Agitate the print in it for 2 minutes. Continue the wash in running tap water for another 2 minutes. A slight fading of the image is normal at this stage; it will darken again in the fixer. The image will then also get a colder tone.

Toning (optional): Some tonings will protect the metallic silver of the image, improving its permanence and reducing its bleaching in the fixer. They also can change the image's tones.
Gold-thiourea toner (L.P. Clerc): 50ml of 1 % gold chloride + 50ml of 1 % thiourea + 0,5gr tartaric acid + 20gr sodium chloride + water to make 1000ml
Palladium toner: 2gr sodium acetate + 2gr citric acid + 400ml DM water + 30 drops of 20 % palladium chloride
Tone the print in either of these solutions until the result pleases you visually; rinse in running tap water for 5 minutes and fix.
Selenium toner: Mix 1 to 5ml of Kodak Rapid Selenium Toner (or equivalent) in 500ml DM water. Can be applied before or after fixing. Be careful: it quickly bleaches the image.
After fixing: 2 minutes, but stop as soon as you notice the image starts to bleach. Then, hypo-clear and wash.
Before fixing: dilute the solution 1:100 or 1:200, tone the print for 30-60 seconds but stop as soon as you notice it starts to bleach; rinse, fix, hypo-clear, wash.
Fixing: Fix = 30gr sodium thiosulphate + 1000ml water. If your water is not alkaline (hard), 2gr of sodium carbonate, or a teaspoon of household ammonia may be added. This will restrain the image's bleaching. Watch out! If the fixer is too alkaline, the elimination of the iron residues risks to be incomplete, and the residual iron (III) will eventually oxidize the silver in the image.
This fixer being very diluted, it will be exhausted quickly. It is advisable to fix in two baths (2

minutes in each) and to replace the second every 8-10 prints. A slight fading of the print in the fixer is no big deal, as the print will dry-down significantly afterwards. On the other hand, it is of utmost importance that all the residual silver is eliminated. Do therefore not interrupt the fixing too early...

Final wash: The purpose of the wash is to eliminate the last residues of the fixer. If you want to accelerate the wash, immerse the print in a 1 % solution of sodium sulphite (or in a half-strength commercial hypo-clear), and wash in running tap water for 20 minutes (without hypo clearing: 30 to 40 minutes).

Problem: the dark parts of the image seem to "bleed" : *a brown cloud streams out the dark areas of the print as soon as it is in contact with the washing water, or with the fix.*
Too much sizing in the paper prevents the sensitizer to impregnate the paper's fibers. Avoid sizing the paper. Too much sensitizer coated on the paper. if necessary: 1st coat, wipe off, dry, 2nd coat, wipe off, dry, expose.
The papier was dried too quickly, the sensitizing solution did not have the time to soak into the paper's fibers.

Problem: stained highlights, print fogged
The alcalinity of the wash development bath caused the formation of metallic compounds which cannot be eliminated: use DM water and citric acid in the first (and if necessary, the second) wash development bath.

Problem: contrast is bad
- Make another negative digitally and adapt the curve of the image: the best guarantee for a good image is a correct negative.
- Overexposing reduces contrasts; underexposing decreases it.
- The paper has to be "bone dry" before exposure; when weather is wet, a simple drying in open air, even for a longer time, might not be enough.
- Expose the paper immediately after drying.
- Replace the classic sensitizer with following "VanDyke FC " (ferric citrate) solution:
Solution A"FC": 35ml water + 10gr ferric citrate + 10gr citric acid + 2,5gr sodium citrate
Add B and C solutions , as for the classic sensitizer.
Use: mix varying proportions of "Classic" (Cl) and "FC" sensitizer :
1Cl + 0FC = 17 steps -- 9Cl + 1FC = 15 steps -- 8Cl + 2Fc = 13 steps -- 5Cl + 5 FC = 12steps. Increasing the FC proportion further will not increase contrast, but reduce speed (longer exposures). Increasing sodium citrate from 2,5gr to 5gr in the 50/50 formula increases contrast by two further steps on a Stouffer step wedge.
- Use Wynn White 's Van Dyke reducer:

potassium ferricyanide 0,25gr
potassium bromide 0,20gr
sodium thiosulphate 5,00gr
DM water to make 1000ml

Soak the print to be reduced in water, make sure no bubbles are left, then immerse and agitate in the reducer. The lighter parts seem to clear first, and contrast increases. Stop before reaching the desired result, rinse, treat for 3 minutes in a hypo clearing solution, wash for 30 minutes. (please note that this is also a solution for cleaning stained highlights...).

Problem: how to decide whether the wash is complete?
If in doubt, a residual hypo test might be helpful:
HypoTest-2: 75ml DM water + 12,5ml acetic acid 28% + 0,75gr silver nitrate + water to make 100ml
After the wash, wipe surface water off a corner of the print with a paper towel (a part that can be hidden or cut off afterwards), then put one drop of HT-2 on it. Let sit exactly for 2 minutes, and blot. If no stain is visible, the wash can be considered complete. It might be a good idea to extend the wash somewhat – say 20 minutes – to make sure. If there is a brown or dark yellow stain, the wash is far from complete. Pale beige means progress, but not enough. Attention! Be aware that the stains are permanent...

D - The Argyrotype Process

Mike Ware, having noticed that none of the iron-silver processes was exempt from traps or difficulties, decided in 1990 to develop a more user friendly technique, and his efforts resulted the year after in a process he called "Argyrotype". While it is quite legitimate to challenge its "historic" character, its filiation with the traditional iron-silver processes nevertheless is quite obvious.
The problem inherent to these last named lies in the use of silver particles, much finer (colloidal silver) than those used in modern silver gelatin emulsions. These particles are also much more vulnerable, which raises enormous problems, and leaves little leeway (neither too much acidity, nor excess of alkalinity..) when processing images. In the argyrotype process, silver nitrate is replaced by silver sulphamate which does not cause any silver degradation in the image and allows for the use of acid (and thus easily eliminated) substances during the development and fixing stages. As silver sulphamate is not readily available and has first to be made, the sensitization procedure is somewhat longer than for the other processes. But after exposure of the negative, the processing is simple as can be: a simple wash and fixing are enough.

Sensitizing bath:

- *prepare following solution:*
  - *. sulphamic acid 7gr*
  - *. silver(I) oxide 7gr*
  - *. ammonium iron(III) citrate, green 22gr*
  - *. Tween 20 ..... 0,2ml*
  - *. water to make 100ml*

  Dilute the sulphamic acid in 70 ml of hot DM water, add little by little the silver oxide with constant stirring until complete dissolution; then add the citrate, without stopping to stir. Let cool down. Mix well the Tween20 in the solution and complete with some DM water at room temperature. If more contrast is wanted, one additional gram of sulphamic acid can be added to the 100ml. If a sediment forms, filter through a coffee filter.
- *or you might order the ready-made solution from Bostick & Sullivan...*

The negative should correspond to one allowing for a correct silver gelatin print on a grade 0 paper. Use a brush reserved for this technique, or a glass rod, to coat the paper. Having applied the emulsion , wait for 3 to 10 minutes, so that the solution has all the time to penetrate the paper. While it is still wet, place the paper between two acetate sheets without scratches, put the negative on top of it and the whole assembly in the printing frame, and finally expose. Ideally, the rate of humidity should be around 40 to 80 %.

Exposure: The Argyrotype process is a POP (printing out process); the aspect of the image appearing after exposure must be relatively close to what the finished image should be. Of course, it still can change during the possible tonings, the fixing and the drying. It is recommended to overexpose slightly.

"Wash development": Begin with a rinse of 10 minutes in demineralized water, with at least one water change during this time. If your tap water is quite hard or chlorinated, this could cause problems for the fixing. It might then be useful to add a little citric acid (or some lemon juice) in the first (demineralized) rinsing water, and to extend your wash for another 10 minutes. If nevertheless problems remain, it will be necessary to resort to a dechlorinator, a chemical sold in stores specializing in aquariums and aquaculture.

Toning (optional): Colors are already influenced by the paper's choice and its rate of humidity in the exposure stage.
As for the other processes, a toning bath not only can modify the color, but also improve its endurance to the fixer, as well as its permanence.
The traditional toner is made from two spare solutions, the first being a 0,2 % gold chloride solution, and the second a 2% ammonium thiocyanate one. Add 50 ml of each in 900ml of demineralized water. This bath is reusable. When it seems to run out, add simply 50ml of both solutions to the old bath: you don't need to start one from scratch!

Fixing: 3 minutes in a 2 % thiosulphate bath. You can extend this time if your print is too dense (overexposed): it will clear up a little. If the print has fine highlight details which have to be preserved, it can be useful to add a teaspoon of liquid ammonia to the fixer. Do not do this if your water is already very alkaline.
It happens that the image begins very quickly to disintegrate in the fixer. This is usually due to the fact that the sensitizer did not penetrate well enough into the fibers of the paper. Adding one drop of Tween20 per 20-24 drops of sensitizer will improve the penetration. Add Tween only at the time of applying the sensitizer, and only to its quantity used for the current image, and not to the whole bottle of spare solution.

Wash: Wash for at least 20-30 minutes in running tap water. The print will turn darker during the drying and return approximately to the tones it had at the time of the wash-development; if a hairdryer is used, it will turn even darker.

Papers: Some papers are not compatible and do not allow satisfactory results: indelible yellow staining, bleeding of the image even when using Tween20, metallised sheen... According to Mike Ware, only pure cotton papers, with an internal Aquapel sizing, free of any other additive, are suitable.
Among the papers giving good results: Bergger COT320, Arches Platine, Herschel Platinotype & Buxton from Ruscombe Mill, Rives BFK, Canson Crob'Art & Fontenay, Whatman's Watercolor.

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Picto Benelux Members' notes:

Notes from Jean Moriau, Thierry Ragogna & René Smets.