## Siderotype Workshop Notes

# Argyrotype

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# Overview of Argyrotype

The Argyrotype process is a latter-day improvement on the late nineteenth century processes of Kallitype, Van Dyke, Sepiaprint, and Brownprint, which were all, in turn, offspring of Sir John Herschel's Argentotype of 1842, the first iron-based silver printing process. The difficulty with these processes lies in clearing the print of iron salts, without dissolving the image silver in the presence of the oxidizing nitrate ion, for which alkaline developers were necessarily recommended, but are not very effective in removing the excess iron(III) salts, which is better done in acid.

The Argyrotype version was devised in 1991, employing an unusual silver salt – silver sulphamate – to avoid the problems of image loss caused by silver nitrate, and to enable mildly acidic (pH 3.5) working conditions. It provides a 'single-bottle' sensitizer solution, having a long shelf-life, a contrast controllable by added acid, and an image colour that can be 'fine-tuned' by the humidity, and the incorporation of a humectant – glycerol. The resulting purplish-brown print of nanoparticle silver has a finer gradation than the traditional iron-silver processes, and good prospects of endurance for a plain paper silver image (which can be notoriously vulnerable) because it is believed to acquire partial sulphide-toning in the processing, which stabilizes the silver. For further information consult: http://www.mikeware.co.uk/mikeware/Argyrotype_Process.html

# Disclaimer

It is the responsibility of the users of chemicals to inform themselves about the risks, and to take appropriate precautions in their handling. Reference should be made to the Materials Safety Data Sheets (MSDS), which are accessible online:

http://www.ilpi.com/msds/index.html

The author hereby denies liability for any consequent sickness, injury, damage or loss resulting from the use of the chemicals named herein.

# Chemicals for Preparing and Processing Argyrotype Sensitizer

**Purity: General Purpose Reagent (GPR) grade *ca.* 98%**

| Substance, Formula | Quantity for 100 cc |
|---|---|
| **Sulphamic acid** $NH_2SO_3H$<br>*aka* amidosulphonic acid, sulfamic acid | 7 g |
| **Silver(I) oxide** $Ag_2O$ | 7 g |
| **Ammonium iron(III) citrate** (green form, *ca.* 16% iron)<br>*aka* ferric ammonium citrate | 22 g |
| **Glycerol** $C_3H_5(OH)_3$<br>*aka* glycerine; 1,2,3-trihydroxypropane; 1,2,3-propanetriol | 1 cc |
| **Water, purified** $H_2O$<br>(distilled, de-ionised, pharmaceutical, etc) to make | 100 cc |
| **Tween 20™** $C_{58}H_{114}O_{26}$<br>*aka* polyoxyethylenesorbitanmonolaurate; polysorbate<br>Separate solution diluted to 10% or 5% v/v | 0.25 cc |

## Processing Solutions:

**Water,** de-chlorinated. Static bath with added citric acid *ca*. 2.5 g/litre

**Sodium thiosulphate** $Na_2S_2O_3$ (hydrated form may be used) 2.5% w/v
Dissolve *ca.* 25 g/litre to process ~10 10x8 in. prints

# Note on Strengths of Solutions

**Meaning of abbreviations:**

**X% w/v** "weight percent volume": **X grams** of solute in 100 cc solution

**Y% v/v** "volume percent volume": **Y cc** of liquid in 100 cc solution

# Apparatus for Preparing Argyrotype Sensitizer

***Apparatus for making 100 cc quantity***

Pyrex glass beaker 200-250 cc

Measuring cylinder 100 cc

Scales or chemical balance sensitive to 0.1 g

Spatula or plastic teaspoon

Glass stirring rod

Conical filter funnel 8-10 cm diameter

Filter paper Whatman Grade #1 15-20 cm diameter

Brown glass bottle 100 cc

Hotplate (or bath of very hot water)

Tungsten lighting to work under, not fluorescent or daylight.

# Equipment and Materials for Coating and Printing Argyrotype

Paper

Glass coating rod or brush

Blotting strips

Syringes, calibrated 2 cc and 5 cc

Glass plate

Spirit level

Drafting tape or clips

Print frame

UVA light source

Timer

Plastic measuring jug 1-2 litre

Stirrer

Processing Dishes (3)

Tongs or plastic gloves

Drying line and pegs or drying screen

# Preparation of Argyrotype Sensitizer

***N.B. This sequence of instructions should be carried out under dim tungsten lighting, not fluorescent or daylight***

**1** Weigh out 7 g of sulphamic acid into a 250 cc pyrex glass beaker.

Add *ca.* 70 cc of pure water (use a measuring cylinder).

Heat to *ca.* 70°C and stir to dissolve the solid completely.

**2** Add 7 g of powdered silver(I) oxide to the hot solution (**1**) in small amounts with vigorous stirring until all is dissolved.

*(This may take up to an hour. If silver(I) oxide is unavailable, it may be prepared as described on p.6.)*

**3** Add 22 g of ammonium iron(III) citrate (the *green* variety: 16% iron) to the warm solution in portions, with stirring, until it is all dissolved. Allow to cool.

**4** Add 1 cc of glycerol to the solution and mix well.

*(This humectant is optional: it improves image colour – see Notes.)*

**5** Add pure water to make up to 100 cc (in a measuring cylinder.)

Filter the solution, using a conical funnel and Whatman grade #1 filter paper, to remove any small amount of solid remaining.

*(The solution should be a clear olive-green colour.)*

**6** Store in a labeled brown bottle in the dark at room temperature.

*(The solution should keep for several years. If it throws down a small amount of black precipitate, it should be re-filtered. The solution is toxic and will stain skin and textiles, etc.)*

***N.B.*** *This argyrotype sensitizer is deliberately made up with a ~20% excess of sulphamic acid (7 g total), The stoicheiometric amount needed to react with 7 g of silver oxide is 5.87 g. The excess acid gives a pH of ~3.5, which suppresses hydrolysis of the iron(III) and helps keep the silver in solution – otherwise silver citrate may precipitate out. This pH is also the optimum for the photosensitivity.*

*Even more sulphamic acid can be added to increase print contrast: it tends to dissolve silver in the highlights. To make a more contrasty sensitizer, dissolve an extra 1 g of solid sulphamic acid in each 100 cc of sensitizer. By mixing this acidified sensitizer with the 'standard' one, the contrast can be 'fine-tuned'.*

*If you should need even less contrast, the figure of 7 g sulphamic acid could be reduced to ~6 g – but it might cause problems of precipitation.*

## Alternative Preparation of Silver(I) Oxide

**a**) Dissolve 2.5 g of sodium hydroxide in *ca.* 40 cc of pure water in a small beaker.

**b**) Dissolve 10.3 g of silver nitrate in *ca*. 40 cc of pure water in a 200-250 cc beaker.

**c**) Add solution (**a**) slowly to solution (**b**), with stirring to precipitate a dark brown sludge of silver(I) oxide (7 g in total).

**d**) Filter off the precipitate with the 8-10 cm conical funnel and 15-20 cm Whatman #1 filter paper.

**e**) Pour pure water onto the precipitate on the filter paper to 'wash' it, three times, allowing it to drain in between.

**f**) Carefully transfer the wet paper and silver oxide sludge to the 250 cc beaker containing the hot sulphamic acid solution in (**1)** on p.5, and stir very gently: the brown precipitate should dissolve easily to a colourless solution. Remove the filter paper with tongs or tweezers when clear of solid, drain, and proceed with step (**3**) on p.5.

# Notes on the Argyrotype Process

## Choice of Paper

The choice of high quality cellulose paper is critical: the best papers of all (naturally!) are Ruscombe Mill's handmade. The following may be tried:

- 'Buxton' or 'Herschel' handmade by Ruscombe Mill
- Atlantis Silversafe Photostore
- Weston Diploma Parchment
- Awagami Masa
- Fabriano 5
- Rives BFK
- Rising Stonehenge
- Cranes Cover or Platinotype

"Acid free" papers containing chalk (calcium carbonate) will perform much better if they are decalcified by soaking in dilute hydrochloric acid (2-5% *v/v*) or sulphamic acid (5-10% *w/v*) for 10 minutes, and washed before coating.

For prints up to 10x8 in. or A4 in size, a paper weight of 160 gsm (grams per square meter, $g/m^2$) is adequate. For larger prints of A3 size, a heavier weight of 240 gsm, or more, will minimise cockling and "bellying" of the coated sheet due to the stresses set up by the hydroexpansion of the cellulose fibres in the wetted area. The sheet will contact the negative better, and be more robust in wet handling.

## Addition of Surfactant to the Sensitizer

The argyrotype sensitizer does not penetrate the cellulose fibres of paper effectively unless a surfactant (wetting agent) is present. A non-ionic surfactant, such as Tween 20™, must therefore be added to the sensitizer before coating to assist its uptake by the paper, and to prevent loss of image substance by "bleeding", if the nanoparticle silver image fails to be retained by the fibres during wet-processing.

The appropriate quantity of this wetting agent will depend on the paper used, but a final concentration of *ca.* 0.5% may be tried as a start. Add one drop (0.05 cc) of a 10% stock solution of Tween 20™ to each cc of sensitizer and mix well before coating.

Tween may interact unfavourably with gelatin-sized papers.

Do not add Tween to the stock sensitizer solution: it doesn't last very well, and the appropriate amount will depend upon the paper.

## Image Colour Improved by Glycerol

The colour of the silver print is determined by the size of the metal particles, which is affected by the humidity of the coating during the printing-out exposure. Higher humidity is promoted by the presence of a hygroscopic substance, glycerol, which is now included in the

sensitizer formulation as a humectant to ensure a pleasing purplish-brown colour. Without it, the image may be a more yellowish-brown.

## Coating

Coating by the rod method (5 or 6 'passes') will require *ca.* 1.5 cc of sensitizer to coat an area appropriate for a 10"x8" print; brush coating consumes more. Blot off any excess sensitizer which may crystallize and damage negatives. Try to "fine tune" your coating volume on the basis of experience, in order to avoid excess. See:

http://www.mikeware.co.uk/mikeware/preparations.html

## Drying

Let the sensitized paper dry uniformly at room temperature and humidity (preferably an ambient RH between 50% and 90%), in the dark for about an hour. Shorter times are possible, but very humid paper may damage precious silver-gelatin negatives, and not lie flat due to fibre swelling. Alternatively, allow a few minutes for the sensitizer to soak in, until the paper surface appears non-reflective, then dry it for about 5 minutes in a stream of warm (40°C) air – the image colour is shifted towards warmer tones by drying. Over-rapid drying may worsen loss of image substance in the wet processing. The sensitized paper is best used within a few hours of coating, although longer term storage in a dark desiccated box is quite possible.

## Printing Exposure and Negatives

Negatives should have a long density range (in the UV): at least 2 and as much as 2.4, to produce a full tonal range in the print – as for my other siderotype processes. Shorter range negatives may be accommodated by using the more contrasty sensitizer recipe. [Indeed, by mixing the two formulations, the contrast of the sensitizer could be 'fine-tuned'.]

Exposure is in the order of five minutes under an average UVA light source. With an 800 W HID UV lamp and digital negatives my exposure time is *ca*. 1 minute.

A hinged-back contact printing frame will enable intermediate inspection of the result; at high RH a detailed print-out image will be obtained: exposure is continued until the high values just appear orange-brown on a yellow background. During processing some more development can be expected to occur and the colour will also darken to a rich mahogany brown in the toner/fixer.

A purplish-grey colour of print-out image may be achieved if the sensitized paper is humidified before exposure by leaving it above water (100% RH) for 30 minutes at room temperature. This is a very economical method of colour control, but a word of caution: humidified sensitized paper can damage a negative during contact printing unless a protective layer of very thin (<20 micron) polyester film is interposed between them.

## Wet Processing Procedure

**1 "Steam":** post-hydration - an optional step **ca. 30 secs**

For the longest tonal range with delicate high value gradations, the exposed print, *before* wet processing, should be left in a humid atmosphere (100% RH) for 30 minutes at *ca.* 20°C, or half a minute over water at 40°C. Overlong "steaming" will cause highlight fog.

**2 Clear:** bath of de-chlorinated water (10 l) + citric acid **2-5 mins**

It is very important to avoid chlorinated water at this stage, when the silver nanoparticles are still highly vulnerable; use rainwater or water that has been passed through an activated charcoal filter, or been boiled and allowed to stand. Add a tablespoonful (*ca.* 25 g) of citric acid to each 10 litres of water to scavenge any traces of chlorine, and to provide slight acidity (pH 4). Alternatively use two baths of smaller volume. Change the first bath for each print. Immerse until the yellow stain is cleared. If there is "bleeding" of nanoparticle silver metal, indicated by a red-brown stain in the wash water and loss of image density, then use more Tween in your sensitizer and process the print face down to minimise staining of adjacent areas.

**3 Tone & Fix:** in 2.5% sodium thiosulphate ***ca.* 2 mins**

Dissolve *ca.* 25 g (1 tablespoonful) of sodium thiosulphate crystals in 1 litre of water. This bath has a capacity of about ten 10x8 in. prints and should be replaced when necessary; do not store and re-use it. The image will intensify as the colour shifts from red to brown, improving the shadow gradation. Overlong treatment in this bath will result in loss of image density especially in the highlights; it will "reduce" an overexposed print, but maybe unevenly.

**4 Wash:** in running water **15-30 mins**

The toned silver image is now less vulnerable to chlorine in the tapwater, but the purer the water, the better. Heavier weight papers require the longer wash.

**5 Drain and Air-dry**: at room temperature.

The image 'dries down' strongly - at least one Zone. Heat drying on a ferrotype plate, or in a heated dry-mount press, or by ironing, may bring about a colour shift to a more neutral blackish brown.

## Permanence & Toning

Like any nanoparticle silver image on plain paper, which lacks a protective organic 'binder' layer, an Argyrotype is inevitably rather vulnerable to aerial attack, especially by oxidizing acids and sulphur-containing substances. However the residual iron and silver in the unexposed areas should be very low and image stability and lightfastness are good.

Modern makers of Kallitypes and Van Dykes seem to agree that toning with platinum, palladium or gold is essential to their preservation, and Argyrotype is in the same category. Like all print-out silver images, the gold toning etc., if desired, should be done *before* the thiosulphate bath, **3**.

The present procedure, however, does not prescribe a toning step for Argyrotypes, because I believe that they already become partially sulphide-toned when they pass through the thiosulphate bath, where the dramatic colour change takes place from yellowish-red to a richer mahogany-brown. This may be due to the yellow silver nanoparticles becoming thinly coated with silver sulphide - only to a depth of a few atoms, perhaps even a monolayer - but sufficient to modify their colour profoundly by its effect on the surface plasmon resonance absorption spectrum. Silver sulphide is very insoluble and stable and should therefore improve the resistance of the image to hostile chemicals. But overlong immersion in thiosulphate completely transforms the silver nanoparticles into silver sulphide, causing the image to become badly faded. Scientific evidence, recently obtained by Ellie Young at the Royal Melbourne Institute of Technology with energy-dispersive X-ray analysis of Argyrotypes, shows the presence of sulphur as well as silver in the image.

Argyrotypes should enjoy a good lifetime without additional toning - but it cannot be guaranteed, because they are silver. Much depends on the care in processing. If permanence is a paramount issue, it is best to print entirely in platinum, palladium, or gold.

# Summary of Argyrotype Procedure

1. **Paper:** choose side, mark up coating area
2. **Sensitizer:** add Tween as required, *ca.* 0.25% v/v
3. **Coat:** ~1.5 cc per 10x8 in. 5 ‘passes’ of rod
4. **Dry:** 1-2 hours at 20ºC or 10 minutes at 40ºC
5. **Negative**: density range ~2 to 2.4 in the UVA
6. **Expose:** UVA source, until high values just visible
7. **“Steam”:** over water: half a min at 40ºC, or ~30 mins at 20ºC
8. **Clear:** in de-chlorinated water + 0.2% citric acid for 2-5 mins
9. **Fix & Tone:** in 2.5% sodium thiosulphate for 1-2 mins
10. **Wash:** in water for 30 minutes
11. **Dry** and press flat