Argyrotype

The Argyrotype Process

By Dr. Michael Ware

Introduction

Within the whole gamut of iron-based processes, printing in platinum, palladium or gold stands supreme for quality and permanence, but the expense of these options deters many practitioners from attempting them. At the other end of the iron-alternative scale is the cyanotype process, providing an image in Prussian Blue: it's truly inexpensive but limited by a colour that is rather strident for some tastes and subject matter. In the centre stand the iron-based silver printing processes, which can aspire to the qualities of platinum without its expense - but also without its certain permanence. Iron-silver processes are useful as an introduction to alternative printing for teaching workshops, for proofing large format negatives, and as a starting point for further toning of the colloidal silver image. It may seem perverse to make silver images on plain paper indirectly, via the photochemistry of iron(III) carboxylates, when they can be made directly by means of the salted-paper process using silver chloride, but the latter is not as simple and straightforward as it is sometimes represented, if a reasonably enduring result is desired.

History

Sir John Herschel, who made so many contributions to photography, was the first to devise an iron-silver process, which he dubbed Argentotype in 1842. Since then there have been many derivatives of his invention: Van Dyke, Kallitype, Sepiaprint, and Brownprint are names known to most of us. Some of these recipes have achieved - for no evident reasons - an almost Byzantine complexity; others are said to be 'deficient in gradation', and most have acquired a rather poor reputation for image stability and permanence. In 'The Complete Photographer' of 1932, R. Child Bayley described his experiences thus: "...a batch of kallitype prints turned out of a drawer the other day bore no sign to distinguish the front of the paper from the back. The image which once had been vigorous enough, had folded its tents like the Arab and had silently stolen away."

In skilled hands, however, there is no doubt that these processes are capable of fine results, and there is no better contemporary source on their practice than Dick Stevens' comprehensive study 'Making Kallitypes - a Definitive Guide', to which I would commend every interested reader. Even Dick Stevens would admit, though, that none of these processes is free from pitfalls or difficulties.

In the interests of achieving a more 'user-friendly' plain paper silver process, I re-visited the underlying chemistry in 1990, and came up with an easier (I don't say "better") process, which I called Argyrotype. This article outlines my chemical reasoning, and describes the details of preparing and processing the sensitized paper.

Structure and Stability of Silver Images

Brown silver images consist of metal particles much smaller than those constituting the black silver images of modern gelatine-silver halide papers; the former have colloidal dimensions (ca. 20nm) - far smaller than the wavelengths of visible light (ca. 500nm) - and their colour is due to a specific absorption of

light which is dependent on their shape, size, state of aggregation and chemical environment. Such small particles are inevitably more vulnerable to chemical attack: they present a relatively large surface area and are rapidly dissolved by reagents that ‘etch’ or ‘bleach’ (i.e. oxidise) silver. The inherent problem of the iron-based silver processes lies in the danger of leaving residual ferric iron in the print - to its ultimate undoing, because iron(III) will oxidise silver with consequent degradation of the image. It is this problem that the Argyrotype process has been designed to avert.

An Alternative Silver Salt

Without exception all the iron-silver processes to date have used the most commonly available soluble salt of the metal, namely silver nitrate. But nitrate is an oxidising anion, and tends to dissolve the colloidal image silver during wet processing, especially under acidic conditions. To minimise this loss of image the Kallitype process employs alkaline-buffered developers of high pH, e.g. Borax. Alas, these create a new problem, because they cause hydrolysis of the excess iron(III) in the sensitizer and the deposition of insoluble ferric hydroxide in the image, which ultimately causes it to fade. In principle the cure is simple: replace silver nitrate with a soluble salt of silver having a non-oxidising anion. There are a few such salts known to chemistry, but most of them, e.g. silver fluoride, have unacceptable properties or a level of toxicity that debar them from ‘home chemistry’. There is, however, a little-known and relatively innocuous silver salt that does fit the bill: Silver Sulphamate, NH_2SO_3Ag. This cannot be bought, but is easily made in situ, as I describe below. It can be employed in an acidic sensitizer of pH 2 to 3, which will wash out of the paper cleanly, without hydrolysis of the excess ferric iron, and without any tendency to dissolve the colloidal silver image.

Chemicals needed for the Sensitizer

Sulphamic acid (spelt ‘sulfamic’ in the USA) NH_2SO_3H .....7 g •
Silver(I) Oxide Ag_2O .....7 g •
Ammonium Iron(III) Citrate (the green form) .....22 g •
Tween 20 (wetting agent; amount variable) .....0.2 cc •
Distilled water to make .....100 cc
GPR (98%) grade of purity is adequate in all cases.

Making up the Sensitizer
(under tungsten lighting only)
1.Heat 70 cc distilled water to 50-60 °C, and dissolve 7 g Sulphamic Acid in it.
2.Add 7 g powdered Silver(I) Oxide to the hot solution (1) in small amounts with vigorous stirring until all is dissolved.
3.Add 22 g Ammonium Iron(III) Citrate (the green variety) in portions to the warm solution (2), stirring until it is all dissolved. Allow to cool.
4.Add 0.2 cc Tween 20 and mix well. (The optimum quantity of this wetting agent will depend on the paper used.)
5.Add distilled water (at room temperature) to make a final volume of 100 cc and filter the solution to remove any small amount of solid remaining. (The solution should be a clear deep olive-green colour.)
6.Store in a brown bottle in the dark at room temperature. (The solution should keep for a year, at least. If it throws down a small amount of black precipitate, it should be re-filtered.)
7.To make a more contrasty sensitizer, dissolve an extra 1 g Sulphamic Acid in 100 cc sensitizer.

Some Alternatives in the Chemistry
If Silver(I) Oxide is difficult to obtain, 8.4 g Silver Carbonate may be used instead; but it should be dissolved at room temperature in a tall vessel - a 250 or 500 cc measuring cylinder to contain the spray; adding the Silver Carbonate in small portions, and allowing the effervescence to die down each time. Alternatively, 7 g Silver(I) Oxide may be precipitated from a solution of 10.3 g Silver Nitrate by adding a solution of 2.5 g Sodium Hydroxide; after filtration and washing, the moist precipitate may be dissolved in the Sulphamic Acid. • If you prefer to avoid the difficulties of obtaining and manipulating the chemicals, then ready made-up Argyrotype sensitizer solution can be purchased from Vintage Image, Fotospeed, Silverprint, Luminos or Bostick & Sullivan.

Choice of Paper
The purity of the paper is crucial to the success of this process. Only the best cotton fibre, internally sized with Aquapel and free of other additives, will do. Papers that I have found to work well are Whatman's Watercolour or Printmaking papers and Atlantis Silversafe Photostore - also made by Whatman - (preferably in the 200 gsm weight); but the best (of course!) is Ruscombe Mill's handmade Buxton paper.
The non-ionic surfactant, Tween 20, is included in the sensitizer formulation to assist uptake of the sensitizer by the cellulose fibres, which minimises "bleeding" of the colloidal metal image during processing, but it may cause uneven penetration of some papers that contain a mixture of fibres. There is always room for experiment with other papers, but you may find that those which do not meet this specification will stain or lose image substance.

Coating
The sensitizer solution can be brushed onto the paper, but this is wasteful, expensive and uneven. It is more economical to coat by means of a glass rod, as I have described in detail elsewhere. About 1.6 cc will be needed to coat a 10"x8". Allow a few minutes for the sensitizer to soak in, until the paper surface appears non-reflective, then dry for about 10 minutes in a stream of warm (40 °C) air. Alternatively, simply allow it to dry at room temperature and humidity for about an hour. The sensitized paper should be used within a few hours, unless a desiccated box is available for longer term storage: shelf life in a dry environment is at least a week.

Printing
As with platinum-palladium printing, a negative having a long density range (ca. 0.2 to 2, or so) is desirable, obtained by overdeveloping by about 70%. Softer 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.]

As with most other alternative processes, the sensitizer is very slow, so printing must be by contact with a large format negative, using an ultra-violet lamp or sunlight, for which the exposure will be comparable with other iron-based processes.

If the humidity of the paper is normal (under an ambient RH between 40% and 80%), a detailed print-out image will be obtained, orange-brown on a yellow background, which gives a good indication of the correct exposure, making test strips unnecessary. A little development (half to one stop) can subsequently be expected to occur in the high values during wet processing, and there will be

considerable ‘dry-down’ of the tonality. Both these factors should be taken into account in judging exposure; the colour will also darken to a rich brown in the fixer bath. It is better to overexpose than underexpose, because a dense image can always be reduced.

Adjustment of Colour

The colour of the print-out image may be shifted to a more neutral tone - an attractive purplish-grey - 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! A word of caution though: humidified sensitized paper can damage negatives during contact printing unless a protective layer of very thin polyester film is interposed between the two, and this may worsen the sharpness of the image.

Wet Processing

Processing is extremely simple and non-critical, requiring only one inexpensive solution, 2% Sodium Thiosulphate, prepared by dissolving about 20 g of the crystals in 1 litre of water. This bath has a capacity of about ten 10"x8" prints and should be replaced when necessary.

1.) Wash the print for 5 minutes in water at room temperature - either running or replaced two or three times (avoid using highly chlorinated water which will damage the silver image). The yellow unexposed sensitizer of excess iron and silver salts should be completely washed out within this time. If there is any ‘bleeding’ of colloidal silver metal, indicated by a red-brown stain running off dense areas of the image, then the paper fibres are failing to trap the colloidal silver particles, and it is likely that insufficient Tween has been used or the paper is unsuitable. The effects of ‘bleeding’ may be minimised by processing the print face down, to avoid staining adjacent areas, but there will be some density loss. If a particularly long tonal range is desired with very delicate high value gradations, the exposed print should be left in a humid atmosphere (100% RH) for ten minutes before wet processing; several steps of highlight detail will build up. Alternatively, you can just breath heavily on it! (The Huurrrotype?)

2.) Fix the print in 2% Sodium Thiosulphate solution for 3 minutes. This removes any traces of insoluble silver salts and intensifies the image: the shadow gradation strengthens, and the colour rapidly shifts from red to brown. Overlong treatment in this bath and exposure to air can result in loss of image density especially in the highlights; this may be used to reduce an overexposed print, or a standard, non-acid fixer may be used. If, on the other hand, very delicate highlight detail is desired, a little ammonia may be added to the clearing bath to make it distinctly alkaline (pH 9 to 10); this inhibits the dissolution of silver, but may raise the level of residual iron in the image.

3.) Wash the print in water for 20 minutes and air dry at room temperature. The image ‘dries down’ significantly - at least one Zone. Heat drying on a ferrotype plate, or by ironing, may shift the colour to a more neutral blackish brown. Unlike silver-gelatine papers, there is no tendency for plain paper prints to curl, and their surfaces are never tacky. Retouching is easily performed on the receptive paper surface with best quality watercolour paints.

Image Permanence

Like any colloidal silver image, especially those on plain paper unprotected by a colloid binder layer, an Argyrotype is inevitably rather susceptible to attack by oxidising 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.

If improved permanence is desired, the image is receptive to the usual toning agents (e.g. selenium or gold), though these may have to be used at a lower concentration than usual. Not having tested them all, I should be glad to hear of people's experience with such toners.

Precautions and Disclaimer

The sensitizer solution is irritant and toxic, and will stain skin and fabrics: wash away any spillages with plenty of cold water. However, it is believed that the rest of this process incurs very little risk. An ultra-violet lamp must of course be shielded from accidental viewing.

References

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