

The New Cyanotype Process

Introduction

The cyanotype process is 153 years old. Can there really be anything new to say about it? You probably know something of its history: invented by Sir John Herschel in 1842, (1) cyanotype was the first successful non-silver photographic printing process. It was used for the first photographically illustrated book, (2) and later became popular with some pictorialists, for whom a commercial paper, called ferro-prussiate, was marketed. (3) Being simple, cheap and fairly permanent, it also enjoyed an extended period of commercial success as the blueprint process for copying drawing-office plans, until it was made obsolete by the invention of dry, plain paper photocopying. The word 'blueprint' still persists in our language, however, with an expanded meaning.

What of the cyanotype process today? It's certainly useful as an inexpensive, easy introduction to hand-coated alternative printing; in my experience, workshop participants feel a good deal more comfortable at the outset, knowing that the sensitizer they are wasting so freely does not cost an arm and a leg. When they've got it under control, they can proceed to platinotype at 20p per drop!

If the growing number of cyanotypes now to be seen on gallery walls and in published commercial work (4) is anything to go by, the process is also providing a significant number of contemporary photographic artists with an expressive medium in its own right, in spite of (or maybe because of) its rather strident colour. The ability to coat this inexpensive sensitizer onto surfaces other than paper, such as wood or textiles, gives it added versatility.

Now, after 150 years of use, you might think that there couldn't possibly be any scope for improving the process; the textbooks (5) commonly recommend essentially the same recipe for pictorial purposes - one that has remained unchanged since the day that Herschel devised it by mixing strong solutions of ammonium iron(III) citrate and potassium ferricyanide. Only the favoured concentrations vary a bit from practitioner to practitioner. There are many up-to-date, accessible accounts of the traditional method, for instance by Hope Kingsley (6) and Terry King (7), so I won't repeat their work here.

What I hope to show in this article is that the process can even now be improved and made more user-friendly, at the cost of rather more chemical manipulation in preparing the sensitizer. But first, let's examine some of the properties of the image substance itself.

The Nature of Prussian Blue

Prussian Blue was first made accidentally in 1704, from ox blood or other animal bits, by near-alchemical procedures (8) that defy my analytical powers. (Vegetarian photographers may be reassured that it is now made quite inorganically.) Although the substance has been studied for over 250 years, chemists have only recently achieved a full understanding of its complex and varied nature. Misconceptions in some older chemistry texts are still being perpetuated in the alternative photographic literature.

Here beginneth the chemistry lesson. Prussian Blue is essentially ferric ferrocyanide, [or Iron(III) Hexacyanoferrate(II) in modern chemspeak] but there exists a whole range of

such iron blues, having compositions depending on their precise method of preparation. (9) At the molecular level, they all have in common a characteristic cubic structure, but this lattice can accommodate variable amounts of water and metal ions within it, so formulae range from $\text{KFe}[\text{Fe}(\text{CN})_6] \cdot 5\text{H}_2\text{O}$ (the so-called "soluble" Prussian Blue) to $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot 15\text{H}_2\text{O}$ ("insoluble" Prussian Blue). (10) In fact, all forms of Prussian Blue are highly insoluble in water; the "solubility" in the former case is an illusion caused by its easy dispersion as tiny (colloidal) particles which form a blue suspension in water, which looks like a true solution. Chemists call this process peptization, and it is responsible for some of the problems that beset the cyanotype process.

By the way, the ability of the Prussian Blue lattice to act as host for relatively large amounts of impurity ions has recently been put to good use by 'locking up' the radioactivity that was deposited on the uplands of North Wales and Cumbria following the Chernobyl disaster. (11) Spreading Prussian Blue on the contaminated soil inhibited the uptake of Caesium 137 by grass; our lamb chops were thus safeguarded from radioactive contamination, but at the price, perhaps, of turning the green hills of Britain to navy blue! Here endeth the whimsical digression.

Although the Prussian Blue pigment of commerce can be made in a form fairly resistant to peptization and destruction by alkalis, (12) the variety produced by the cyanotype process is unfortunately -and inevitably- the "soluble" form. It is therefore rather easily washed out of the paper and 'bleached' by strong alkali, which converts it to very weakly coloured salts of iron.

Disadvantages of the Traditional Process

As an occasional user of cyanotype, I found that the traditional method seemed to suffer from some irksome features - or was it just my incompetence? If, gentle reader, you have already tried the process, see if you agree with me that:-

1. Printing can be rather slow compared with other iron-based processes such as the palladiotype; exposures of thirty minutes or more to a typical UV light source are not unusual.
2. The two ingredients have to be stored separately, and the solution of Ammonium Iron(III) Citrate provides an excellent nutrient for mould growth, so that after a month or two, it can come to resemble one of Prof. Quatermass's more bizarre experiments (13).
3. The sensitizer is often not well-absorbed by the paper and some tends to lie on the surface; being hygroscopic, it causes a tackiness which can wreck your negative.
4. It is disappointing to watch your picture gurgling down the sink as large amounts of the image substance, "soluble" Prussian Blue, wash out during the wet processing. Heavy overexposure is usually recommended as the only remedy for this drastic weakening of the image.
5. Stained highlights are quite common, due to inadequate clearing and 'bleeding' of the Prussian Blue; they may be difficult to wash out without losing gradation in the high values.

If you agree with me about most of these disadvantages, then there is some point in your reading on.

A Chemical Solution

The first three disadvantages could be overcome by using Ammonium Iron(III) Oxalate instead of the citrate, because

1. It is more light sensitive.
2. It is not attacked by mould.
3. Its solution penetrates the paper fibres more readily (see my article on Paper).

But Ammonium Iron(III) Oxalate also causes a chemical problem, because when it is mixed with Potassium Ferricyanide to prepare the sensitizer solution, the sparingly soluble salt, Potassium Iron(III) Oxalate, crystallises out. A 'gritty' sensitizer is useless, and if this happens within the sensitized paper it can cause quite pretty, but totally unwanted fern-like patterns. The answer to the problem would be to use Ammonium Ferricyanide instead of the Potassium salt, but this is unobtainable (so far as I know) and rather troublesome to make.

Disadvantages (4) and (5) are due to the fact, already stated, that the cyanotype process produces the so-called "soluble" form of Prussian Blue. Substitution of ammonium ions for potassium ions in the structure would have the benefit of diminishing this tendency, yielding an "ammonium blue" of good colour, which is more resistant to peptization and alkalies.

All these problems (1) to (5) can therefore be overcome by the simple trick of eliminating most of the potassium ions from the sensitizer; this is achieved by adding finely ground solid Potassium Ferricyanide to an appropriate excess of a very concentrated solution of Ammonium Iron(III) Oxalate, allowing it to crystallise then filtering off and rejecting the solid Potassium Iron(III) Oxalate that results. The biggest objection to this procedure is the present artificially high cost of Ammonium Iron(III) Oxalate, but cheaper sources of this chemical are now becoming available. The 'user friendly' sensitizer is a single solution with a very good shelf life, and it provides excellent image quality.

The following recipe is not engraved on tablets of stone; it has given the author very satisfactory results so far, but deserves to be more extensively tested, and may yet allow room for improvement by fine-tuning the concentrations.

Sensitizer Chemicals needed

- * Ammonium Iron(III) Oxalate $(\text{NH}_4)_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ 30 g
- * Potassium Ferricyanide $\text{K}_3[\text{Fe}(\text{CN})_6]$ 10 g
- * Ammonium Dichromate $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ (25% solution)0.5 cc
- * Distilled water to make100 cc

GPR Grade (98-99%) purity is adequate.

Preparation of Sensitizer

The preparation of this sensitizer solution calls for a bit more experience in chemical manipulation than is required to make a traditional cyanotype sensitizer, so don't undertake it unless you are fairly confident. This work should be carried out under tungsten light, not fluorescent or daylight.

Please note that all the chemicals are poisonous!

1. Using a pestle and mortar, finely powder 10 g Potassium Ferricyanide. Wear a dust mask, to avoid inhalation of the powder, and pay attention to thoroughly completing this step, which is indicated when all the red crystals are crushed to a yellow powder.
2. Heat ca. 30 cc distilled water to ca. 50 °C and dissolve in it 30 g Ammonium Iron(III) Oxalate.
3. Add 0.5 cc 25% Ammonium Dichromate solution, (previously prepared by dissolving 5 g of the solid in distilled water and making up to a final volume of 20 cc). Mix thoroughly.
4. To the solution, while it is still hot, add the 10 g of finely powdered Potassium Ferricyanide in small portions with vigorous stirring; few (or preferably no) red crystals should be seen, and green crystals will begin to appear. Set the solution aside in a dark place to cool and crystallise for about one hour.
5. Separate most of the liquid from the green crystals by filtration. The green solid (Potassium Iron(III) Oxalate) is disposed of safely (poisonous!). The volume of solution extracted should be ca. 30 to 33 cc.
6. Make up the olive-yellow coloured solution with distilled water to a final volume of 100 cc. The sensitizer can be made more dilute (e.g. up to 200 cc): it will be faster to print, but yield a less intense blue.
7. Filter the sensitizer solution and store it in a brown bottle kept in the dark; its shelf life should be at least a year.

Use of Wetting Agent

With some papers the use of a wetting agent can greatly improve the ease of coating and the retention of Prussian Blue by the paper fibres. I prefer Tween 20 (polyoxyethylene sorbitan monolaurate - a non-ionic surfactant) which may be added to the sensitizer solution to produce a final concentration of ca. 0.1 to 0.5%. A stock solution of concentration 2% is useful for this: if you find it necessary, add one or two drops per cc of sensitizer and mix well just before coating. The appropriate amount will depend upon the paper, so it is better not to add it to the bulk of the stock sensitizer solution unless you're certain what paper is to be used: Tween 20 is very suitable for Silversafe and Buxton papers, but may interact unfavourably with gelatin-sized papers.

Choice of Papers

The cyanotype sensitizer is a delicate test of paper quality - especially if the coated paper is left for some hours in the dark at normal relative humidity: any change of the bright

yellow coating towards a green or, worse, blue colour is an indication of impurities or additives in the paper that are hostile to this process (and possibly to other processes as well). I recommend Atlantis Silversafe Photostore 200 gsm, Arches Platine 310 gsm, and Whatman Watercolour 290 gsm; but the best results (of course!) are obtained on Ruscombe Mill's handmade 'Buxton' paper, (see my article on paper).

Coating Techniques

Coating by the rod method will require approximately 1.5 cc of sensitizer for a 10"x8"; brush coating consumes more, but try to avoid excess sensitizer which may puddle and crystallise. I have to remind you that this sensitizer solution is toxic if ingested (much more so than traditional cyanotype) and it will obviously stain skin, wood, clothes, textiles, household pets and any other absorbent surfaces.

Drying

It is simplest to let the sensitized paper dry at room temperature in the dark for about one hour; but there will be no difference if you prefer heat-drying at about 40°C for 10 minutes. Expose the sensitized paper within a few hours of coating, if possible. Its storage life depends on the purity of the paper base, as mentioned above; it will keep longer in a desiccated enclosure. The coated side should remain light yellow: if it has turned green or blue reject it, because the highlights will be chemically fogged, and look for a better paper.

Negatives

For a full tonal range in the print, the negative should have a long density range of at least 1.8, like those for platinum-palladium printing; i.e. extending from base+fog at around 0.2 to a Dmax of 2 or more. This is achieved by "overdeveloping" the negative to the extent of 70%-80%.

The contrast of the sensitizer can be lessened by adding citric acid, so that it can even accommodate a negative density range of 2.6 or so. Conversely, the contrast can be increased by the addition of more ammonium dichromate solution.

Unlike the traditional cyanotype sensitizer, I have not encountered any problems with this sensitizer damaging negatives during contact printing.

Exposure

Whether the light source is the sun or a UV lamp, exposure is much shorter than that needed for the traditional Cyanotype recipes - this new sensitizer requires about five minutes exposure under an average light source.

Since this is a print-out process, a traditional hinged-back contact printing frame should be used; the image can then be inspected without losing registration and the correct exposure reached without the need for preliminary test strips. The exposure is continued until the high values just appear green, the mid-tones are blue, and the shadow tones are substantially reversed to a pale grey-blue, giving the image a "solarised" look.

If you do not mask your negative when printing (with ruby lith tape, for instance) but expose the entire coated area, then you will never know if the print is properly cleared. This is the disadvantage of 'showing the brushmarks' to prove it's a handmade print.

Wet Processing

You can process the exposed paper most simply with nothing more than a few changes of water, but a better gradation with stronger shadow tones is obtained if it is treated initially in a bath of citric acid solution (strength 1% to 2%) for 10 minutes. This bath should be replaced after a few prints have passed through it: typically, 1 litre will process ten 10"x8" prints. The yellow stain of sensitizer should clear completely from unexposed areas - it is worth holding the print up to a bluish light to check that no yellow stain remains in the interior of the paper; if the stain persists, use a second citric acid bath. Finally wash gently in running water for about 20 minutes. Unlike prints made by the traditional recipe, there should be very little loss of image substance during this procedure.

The reversed shadow tones usually regain their full values quite rapidly during the wet processing, but if not they will do so during drying (24 hours). However, if you're anxious to see the final result immediately, then immerse the print in a bath of 0.3% hydrogen peroxide (50 cc of the 6% solution -so-called "20 volume"- diluted to 1 litre of water) for no more than half a minute. This treatment makes no difference to the final result.