Siderotype Workshop Notes

New Cyanotype

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Overview of Cyanotype

Sir John Herschel invented the cyanotype process in 1842, and it has been practised essentially unchanged ever since, becoming known after his death in 1871 as the commercial Blueprint, the first reprographic process. This method is the oldest, simplest, safest, and cheapest of all alternative photographic printing process - but not the best in image quality. The drawbacks of the traditional cyanotype process (inconsistent chemicals, short-lived sensitizer, poor absorption by paper, loss of image substance in wet-processing, limited exposure range, poor tonal gradation, slow printing speed) were overcome in 1995 with Mike Ware's chemically up-dated version, named 'New Cyanotype' in honour of Herschel's original innovation.

The new formula, once made up, provides a convenient 'single-bottle' sensitizer solution having a very long shelf-life. Requiring only a short UV exposure, the process yields an image in stable Prussian blue pigment displaying a smoothly graduated tonal scale and excellent colour on a matte paper surface, and having a maximum density verging on black. The wet-processing is extremely simple, non-critical, and offers a degree of contrast control. The image colour may be easily modified by a variety of toning agents, and the inexpensive sensitizer may also be applied to fabrics and other surfaces. For further information consult:
http://www.mikeware.co.uk/mikeware/New_Cyanotype_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 New Cyanotype Sensitizer

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

Substance and Formula	**Quantity for 100 cc**
Potassium ferricyanide $K_3[Fe(CN)_6]$ *aka* potassium hexacyanoferrate(III)	10 g
Ammonium iron(III) oxalate $(NH_4)_3[Fe(C_2O_4)_3].3H_2O$ *aka* ferric ammonium oxalate, ammonium ferric oxalate	30 g
Ammonium dichromate $(NH_4)_2Cr_2O_7$ (OPTIONAL) *aka* ammonium bichromate	0.1 g
Water, purified, H_2O (distilled, de-ionised, pharmaceutical, etc) to make	100 cc
Tween 20™ $C_{58}H_{114}O_{26}$ (OPTIONAL) *aka* polyoxyethylenesorbitanmonolaurate, polysorbate	0.25 cc
Citric acid $C(OH)COOH.(CH_2COOH)_2$ (OPTIONAL) *aka* 2-hydroxypropane-1,2,3-tricarboxylic acid	2 g

Processing Solutions:	**Quantity for *ca.* 60 10x8 in. prints**
One of the following (in order of preference)**:**	
Nitric acid HNO_3 0.25% to 1% v/v 100 cc of conc. (65%) HNO_3: dilute 2.5-10 cc to 1 litre	10 litres
Hydrochloric acid HCl 0.25% to 1% v/v 100 cc of conc. (37%) HCl: dilute 2.5-10 cc to 1 litre	10 litres
Citric acid 5% w/v 500 g needed: dissolve 50 g in 1 litre of water	10 litres
Hydrogen peroxide H_2O_2 0.3% (OPTIONAL) 500 cc of 6% ("20 Volume"): dilute 50 cc to 1 litre	10 litres

Chemicals for toning Cyanotypes

Ammonium hydroxide NH_4OH 1% v/v
Dilute 10 cc of concentrated (~27%) ammonia to 1 litre

Sodium carbonate Na_2CO_3 (can be hydrated form) 5% w/v
Dissolve 50 g in 1 litre of water

Tannic acid $C_{76}H_{52}O_{46}$ 1% w/v
Dissolve 10 g in 1 litre of water

Acetic acid CH_3COOH 1% v/v
Dilute 10 cc of concentrated (~90%) acetic acid to 1 litre

Lead(II) acetate $Pb(OCOCH_3)_2.3H_2O$ 5% w/v
Dissolve 50 g in 1 litre of water

Trisodium phosphate Na_3PO_4 (can be hydrated form) 5% w/v
Dissolve 50 g in 1 litre of water

Nickel sulphate $NiSO_4.6H_2O$ 5% w/v
Dissolve 50 g in 1 litre of water

Note on Strengths of Solutions

Meaning of abbreviations:

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

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

Apparatus for Preparing New Cyanotype Sensitizer

Apparatus for making 100 cc quantity

Pyrex glass beakers 2 x 100 cc

Measuring cylinder 100 cc

Scales or chemical balance sensitive to 0.1 g

Glass stirring rod

Conical filter funnel *ca.* 8–10 cm diameter

Filter paper Whatman Grade 1 *ca*. 15–20 cm diameter

Brown glass bottle 100 cc

Hotplate (or bath of very hot water)

Thermometer 0–100 ºC

Tungsten lighting to work under, not fluorescent or daylight.

Equipment and Materials for Coating and Printing New Cyanotypes

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 (2)

Tongs or plastic gloves

Drying line and pegs or drying screen

Preparation of New Cyanotype Sensitizer

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

1 Weigh 10 g of potassium ferricyanide into a small (100 cc) pyrex glass beaker.

Add exactly 20 cc of purified water (use a measuring cylinder).

Heat (*about* 70°C) and stir well until the solid is dissolved.

Keep the solution hot.

(A thermostatted hotplate is best for heating the solutions, but a basin of very hot water will do. Dissolution may be slow if crystals are large – a mechanical stirrer is recommended.)

2 Weigh 30 g of ammonium iron(III) oxalate into a second (100 cc) pyrex glass beaker.

Add exactly 30 cc of purified water (use a measuring cylinder).

Heat (*about* 50°C) and stir until the green solid is dissolved.

(Ignore any small residual impurity of colourless crystals.)

Add 0.1 g of ammonium dichromate and let it dissolve.

(The small amount of ammonium dichromate may be omitted, but the contrast and shelf-life of the sensitizer will be diminished.)

3 Add the hot potassium ferricyanide solution (**1**) to the ammonium iron(III) oxalate solution (**2**), stir well, and set the mixture aside in a dark place to cool to room temperature (~20°C) and crystallize.

(For this quantity of solution, the cooling and crystallization will take at least two hours, but it may be better left overnight, especially if a larger scale of preparation is used.)

4 Separate the green liquid from the green crystals by decanting and filtration: use a conical filter funnel with a Whatman grade 1 filter paper, running into a 100 cc measuring cylinder.

(A coffee filter will do. The volume of filtrate should be ca. 62 cc. The yield of green crystals should be ca. 15 g. Dispose of these crystals safely by washing away with hot running water.)

5 Make up the filtered solution with purified water to a final volume of 100 cc in the measuring cylinder. Mix well.

Transfer the sensitizer solution to a well-stoppered, labelled and dated brown bottle.

(The sensitizer solution is toxic if ingested and it will stain skin, etc. Stored in a cool dark place, its shelf-life is at least a year.)

Notes on the New Cyanotype Process

Choice of Paper

Use only papers that are ***not*** alkaline-buffered with chalk (calcium carbonate). Alkalies are hostile to cyanotype chemistry. The best results will be obtained on unbuffered papers such as:

- 'Buxton' or 'Herschel' Handmade by Ruscombe Mill
- Weston Diploma Parchment
- Canson Lavis Technique
- Crane's Platinotype
- Atlantis Silversafe Photostore
- Arches Platine

If buffered papers are unavoidable, such as Fabriano Artistico, Canson Montval, or Whatman Watercolour, they should be pre-treated in a bath of dilute (5% v/v) hydrochloric acid, or 5-10% sulphamic acid, to destroy the chalk, then washed. The new cyanotype sensitizer is a sensitive test of paper quality: any change, in the dark, of the bright yellow coating to green or blue signals impurities or undesirable additives in the paper.

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 Citric Acid to the Sensitizer

Chemical fogging ("greening") of the coating due to paper impurities may often be prevented by adding citric acid to the sensitizer, before coating, to a final concentration of *ca*. 2%. Add one drop (0.05 cc) of a 40% solution of citric acid per cc of sensitizer. Do not add citric acid to the stock of sensitizer, because it will shorten the shelf-life.

Addition of Surfactant to the Sensitizer

The new cyanotype sensitizer penetrates cellulose fibres well, and absorbent papers may not require any additional surfactant (wetting agent), but some hard-sized papers, such as Buxton, may yield a better, more uniform coating if a surfactant is used.

Tween 20™ (a non-ionic surfactant) should be added to the sensitizer solution before coating to produce a final concentration of *ca.* 0.25%. E.g. you can add one drop (*ca.* 0.05 cc) of a 5% stock solution of Tween 20™ to each cc of sensitizer and mix well.

Do not add Tween to the stock sensitizer solution: it doesn't last very well, and the appropriate amount will depend upon the paper. Tween may interact unfavourably with gelatin-sized papers.

Coating

Coating by the rod method (4 or 5 '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. For instructions see:

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

Drying

Let the sensitized paper dry at room temperature in the dark for about an hour. Shorter drying 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 heat-dry it with an air stream at about 40°C for *about* 5 minutes. The dryness of a cyanotype paper does not appear to influence image colour or contrast – the only difference may be that rapid drying can reduce any chemical fogging due to impurity; but note that over-rapid drying may worsen the loss of image substance during the wet-processing procedure.

The storage life of coated paper depends on the purity of the paper base, as mentioned above, so use the sensitized paper within a few hours of coating, if possible. It will keep longer in a cool, dark desiccated enclosure. The coated side should remain light yellow: if it turns green or blue the highlights are chemically fogged, so either reject it and find a better paper, or try adding citric acid as described above, for your next coatings.

Printing Exposure and Negatives

Negatives should have a long density range (in the UV): at least 1.8 and as much as 2.4, to produce a full tonal range in the print – as for my other siderotype processes.

Exposure is much shorter than that needed for the traditional Cyanotype process – probably less than five minutes under an average UVA light source. With an 800 W HID UV lamp and digital negatives my exposure time is *about* 60 seconds.

Since this is substantially a print-out process, a traditional hinged-back contact printing frame will enable inspection of the desired result: the exposure is continued until the high values appear green, the mid-tones are blue, and the deepest shadow tones are reversed to a pale blue-grey, giving the image a 'solarised' look.

Wet Processing and Contrast Control

1 Acidic Development: immerse the exposed print in a bath of dilute nitric acid (*ca.* 0.25%–1% v/v) for 5–10 minutes.

(For safety in handling, it is suggested that a stock solution of 10% v/v nitric acid is made up, by diluting the concentrated (~65% w/v) acid (Care: corrosive, fumes!) 10-fold (*i.e.* 100 cc to 1 litre). This is then diluted a further 10–40 times before use. The final 100–400x diluted bath is not dangerous.)

The strength of this acid bath, at the development stage, offers a means of controlling print contrast, which is higher for stronger (1%) acid and lower for weaker (0.25%) acid. The softest gradation can be obtained by omitting the acid altogether, and processing the print initially in a bath of non-alkaline water, but this will give a reduced maximum density. The yellow stain of residual sensitizer should be seen to clear completely from unexposed areas.

Some runoff of Prussian blue builds up in the bath: it should not be re-used, otherwise blue staining may occur. The development bath should be replaced after a few prints have passed through it: typically, 1 litre will process six to ten 10"x8" prints.

If there are safety objections to using nitric acid, then 0.25%–1% v/v hydrochloric acid may be used. If there are safety objections to this, then 5%–10% w/v sulphamic acid could be used, or as a last resort, 1%–5% w/v citric acid. Acetic acid is not recommended.

2 Water Wash: immerse in gently running water for *about* 30 minutes.

Alkaline water (pH >7) must not be used, nor hard water, containing calcium salts, which will damage the Prussian blue image. Alternatively, at least three static baths of acidic water may be used.

The reversed shadow tones will rapidly regain their full density during the development in nitric acid; if this has not been used, then they will be restored slowly by air oxidation during drying (24 hours). 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 diluted 20x to 1 litre of water) for no more than half a minute during washing. This treatment makes no difference to the final result.

Permanence & Stability

The Prussian blue pigment of Cyanotypes is destroyed by alkali: buffered wrappings and mounts (pH >9) should therefore be avoided. Cyanotypes can fade somewhat in bright daylight, but this recovers on dark storage in the air, and they should regain their density fully after a few days. Exhibition under low light levels causes no measurable fading. For conservation information see:

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

Summary of New Cyanotype Procedure

1. **Unbuffered paper:** choose side, mark up coating area
2. **Prepare sensitizer:** add citric acid (to 2%) and/or Tween (to 0.25%), if needed
3. **Coat:** *ca.* 1.5 cc per 10x8 in. area: 5–7 'passes' of coating rod
4. **Dry:** 1–2 hours at room temperature, or hot air for 10 minutes
5. **Negative**: density range ~2–2.4 in the UVA
6. **Expose: UVA** source till highlights green and shadows 'reversed'
7. **Develop:** 0.25–1% v/v nitric acid according to contrast desired; (concentrated nitric acid diluted 400–100x) for 5–10 minutes
8. **Wash:** in non-alkaline water for 20–30 minutes
9. **Drain** for 10 minutes and **Dry** flat

Toning Cyanotypes

Purplish-brown – Tannic acid

1 If the print is dry, presoak it in water for 1 minute.

2 Immerse the print in 1% v/v ammonia (ammonium hydroxide) for *ca.* 5 minutes until the Prussian blue image is bleached to pale yellow (ferric hydroxide). Caustic soda or caustic potash (sodium or potassium hydroxide) 1% w/v, or domestic washing soda (sodium carbonate) *ca.* 5% w/v, can be used instead of ammonia.

3 Rinse in water for half a minute.

4 Immerse in 1% v/v acetic acid for one minute to neutralise any residual alkali.

5 Rinse in water for half a minute.

6 Tone in 1% Tannic acid solution for 5 to 10 minutes.

7 Wash in water for 20 minutes.

Shortening the time in **2** can yield interesting split-tone effects.

This treatment generally intensifies the image, and imparts a rich purplish-brown colour. Staining of the paper base is a problem, however, and the colour is very sensitive to alkali.

Yellow – Trisodium phosphate

Immerse a heavily printed cyanotype in a bath of 5% w/v trisodium phosphate solution, to bleach it to a golden yellow colour – probably iron(III) phosphate, a fairly stable pigment.

Violet – Lead(II) acetate

Make up a 5% w/v solution of Lead(II) acetate and adjust its pH to 7.5 to 8 by adding a little ammonia to it – use a pH paper to check. (A slight precipitate doesn't matter, it can always be filtered off.)

This bath will transform a new cyanotype to a beautiful violet-blue in one or two minutes at room temperature. The colour is permanent and stabilises the Prussian blue against light fading.

Lead(II) acetate is a seriously toxic heavy metal salt. Guard it well.

Greenish-blue – Nickel(II) sulphate

Immerse the cyanotype in a 5–10% solution of a nickel(II) salt (e.g. the sulphate, chloride or nitrate) for an hour or so. The colour shift with nickel(II) salts is rather slight – towards a more greenish-blue.

This treatment has the beneficial effect of making the cyanotype much more resistant to alkaline hydrolysis.

Nickel(II) salts are listed carcinogens. Consult the MSDS.

For more information on toning cyanotypes and examples see: http://www.siderotype.com/pdf/sid_contents.pdf