Simple Cyanotype

Preparation of Sensitizers

and

Instructions for their Use

One-bottle and Two-bottle versions with contrast control

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Introducing Three Varieties of Cyanotype

The 'Classic' method of cyanotype invented by Sir John Herschel in 1842 has been practised essentially unchanged ever since. It is the oldest, simplest, safest, and cheapest of all alternative photographic printing processes – but not the best in image quality. The drawbacks of the 'Classic' formula are due to wide variability in the composition of the sensitizer chemical, ferric ammonium citrate, *aka* ammonium iron(III) citrate: it may be poorly absorbed by paper, losing image substance during wet-processing, which causes a limited exposure scale with poor tonal gradation. These problems were overcome in 1995 by my chemically up-dated version, named 'New Cyanotype', which employs pure ammonium ferric oxalate to provide a convenient single-bottle sensitizer, having a shelf-life of years with dichromate as a preservative. The 'New' formula only requires a much shorter UV exposure (~1/8th) and yields a Prussian blue image with a long, smooth tonal scale of excellent colour, having a maximum density verging on black (1.7). The wet-processing is simple and offers some control of contrast. For further information consult *Cyanomicon* at:

https://www.mikeware.co.uk/mikeware/downloads.html

Preparation of the 'New' formula does call for some experience in manipulative chemistry. That is not required for this latest version, called 'Simple Cyanotype', which avoids commercial ferric ammonium citrate altogether but effectively makes it *in situ*, easily and cheaply, from widely-available pure chemicals. Unlike 'New', the 'Simple' sensitizer contains no toxic dichromates or oxalates, making it safer for children and the environment. It is faster than an average 'Classic' formula, but still slower than 'New'. It has excellent tonal separation with a high D_{max} of ~1.5 and it can provide an exposure scale varying from 2.7 to 1.4 depending on the sensitizer formula, so the contrast can be fine-tuned to match widely differing negatives – an innovation not hitherto possible with cyanotype. It can be made up as a one-bottle or two-bottle sensitizer, depending on the duration of use.

Chemicals needed for Preparing and Processing Simple Cyanotype Sensitizers

Purity: Reagent grade ~98% is preferred, where possible.
Use only fine chemicals from reputable suppliers.

Substance & Formula	**Quantity for 100 cc**
	Sufficient to coat ~60 10x8 in. prints
Citric acid monohydrate $C(OH)COOH.(CH_2COOH)_2.H_2O$	13 g
aka 2-hydroxypropane-1,2,3-tricarboxylic acid	
OR Citric acid anhydrous $C(OH)COOH.(CH_2COOH)_2$	12 g
Iron(III) nitrate nonahydrate $Fe(NO_3)_3.9H_2O$	12 g
aka ferric nitrate nonahydrate	
Warning: this salt is highly deliquescent: any absorbed water will react and destroy it irreversibly. Keep it well dehydrated and do not expose to the atmosphere unnecessarily	
Ammonia solution NH_3 (supplied in various concentrations)	
aka ammonium hydroxide NH_4OH	
10% *w/w* (S.G. 0.959) (only for single-bottle sensitizers)	~50 cc
Warning: such commercial brands of 'household ammonia' *may* contain additives that spoil the chemistry	
Preferably use one of the more concentrated laboratory reagents:	
24% *w/w* (S.G. 0.912) 25% *w/w* (S.G. 0.909)	
28% *w/w* (S.G. 0.900) 30% *w/w* (S.G. 0.894)	
32% *w/w* (S.G. 0.890) 35% *w/w* (S.G. 0.880)	~20 cc
Concentration may easily be checked with a hydrometer	
Potassium ferricyanide $K_3Fe(CN)_6$ 99% purity is desirable	10 g
aka potassium hexacyanoferrate(III)	
Water, purified, H_2O	100 cc
(distilled, de-ionised, pharmaceutical, etc.) to make	
Tween 20™ $C_{58}H_{114}O_{26}$	~1 cc
aka polyoxyethylene sorbitan monolaurate; polysorbate	

Processing Solution:	**Quantity for ~60 10x8 in. prints**
Citric acid (as above – either variety)	200 g
To make ~1% w/v solution dissolve 10 g in 1 litre of water. More dilute may be preferred to lessen blue in highlights. Use to process 2 or 3 prints only.	

Safety in Preparation

PROTECT YOUR EYES with safety goggles.
Avoid inhaling ammonia vapour!
Gloves are advisable for preparation, but not for use.

Apparatus for Preparing the Sensitizers

Scales or balance sensitive to 0.1 g

Glass beaker 200+ cc

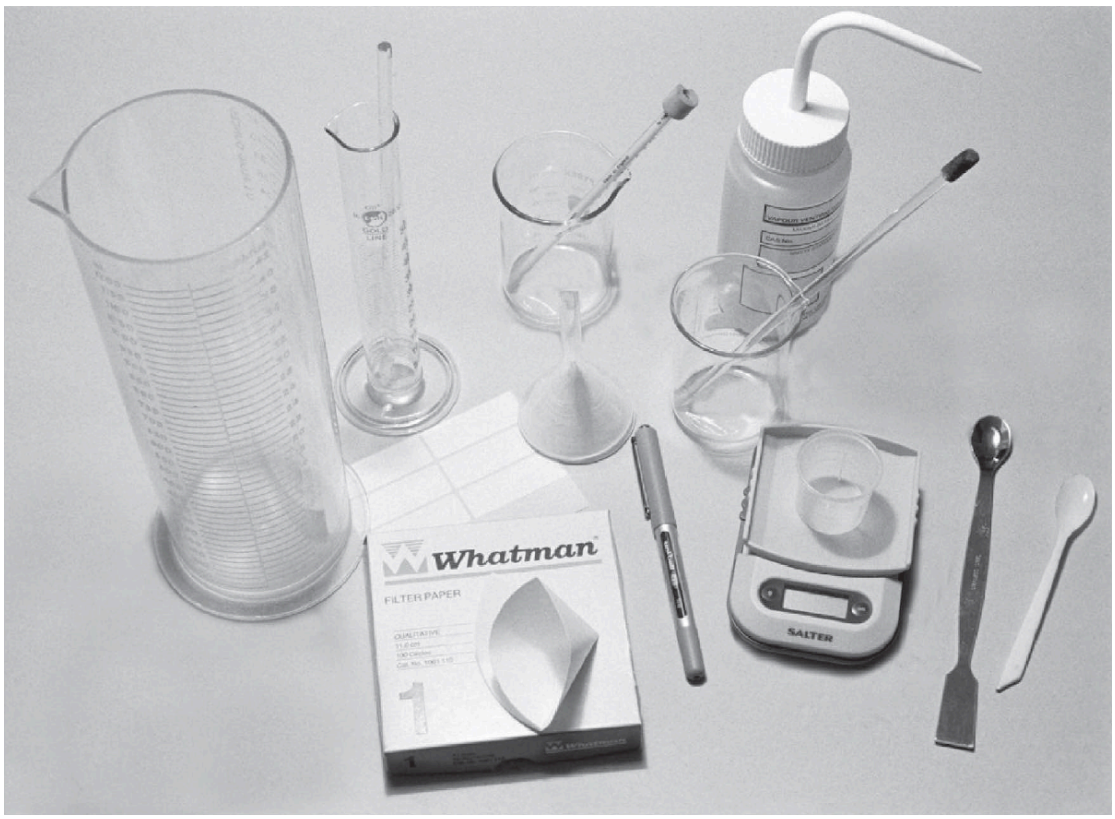
Measuring cylinder (US: “graduate”) 100 cc

Glass stirring rod or magnetic stirrer and ‘follower’ bar

Brown glass bottle 100 cc

Filter funnel and filter paper

Tungsten or LED lighting to work under, not fluorescent or daylight.



Illustrative of typical equipment – not all required here

Preparation of 'One-bottle' Sensitizer A

Purity: If high photochemical precision is an issue, use Analytical Reagent (AR) grade chemicals, purity 99%+, and weigh to ±0.1 g.
N.B. All the following instructions must be carried out under dim tungsten or LED lighting, not fluorescent tubes or daylight.

A. Low Contrast: Exposure Scale ~2.7

1) Weigh out 13 g of citric acid monohydrate into a 200+ cc beaker.
OR 12 g of citric acid anhydrous.

Add 35 cc of pure water, and stir to dissolve all the solid.

2) Weigh out 12 g of iron(III) nitrate nonahydrate. **Immediately** add the solid to solution **1)** in portions, stirring to dissolve it.

3) Use a measuring cylinder (US "graduate"), or preferably a graduated pipette, to measure out:

33.0 cc of 10% *w/w* ammonia solution.
OR 14.5 cc of 24% *w/w* ammonia made up to 33 cc with water.
OR 13.9 cc of 25% " "
OR 12.6 cc of 28% " "
OR 11.8 cc of 30% " "
OR 11.1 cc of 32% " "
OR 10.3 cc of 35% " "

Add it to **2)** slowly with stirring; the yellow solution turns green.

4) Weigh out 10 g of potassium ferricyanide, purity 99% preferably.

Add the solid to **3)** and stir thoroughly to dissolve all the crystals.

5) Transfer solution **4)** to a measuring cylinder or volumetric flask and make it up with pure water to a final volume of 100 cc and mix well. Transfer the solution to a well-stoppered brown glass bottle. Label and date it, and store in the dark, preferably at low temperature.

The solution should be left to stand overnight before first use. Any trace impurities in the chemicals may cause the precipitation of a very small amount of sediment – brown ferric hydroxide and/or Prussian blue – which can be removed by filtration if necessary.

N.B. This sensitizer has a storage life of several weeks at room temperature but will keep much longer if refrigerated to *ca.* 5°C. If stability and storage life are an issue, you are recommended to use the 'Two-bottle' option to make up the sensitizer, as on p.7.

Preparation of 'One-bottle' Sensitizers B & C

B. Medium Contrast: Exposure Scale ~2.3

1) & **2)** Follow these steps as in **A** above, then substitute the following for **3)**:

3) Use a measuring cylinder (US: "graduate"), or preferably a graduated pipette, to measure out:

38.5 cc of 10% *w/w* ammonia solution.
OR 16.9 cc of 24% *w/w* ammonia made up to 38.5 cc with water.
OR 16.2 cc of 25% " "
OR 14.7 cc of 28% " "
OR 13.8 cc of 30% " "
OR 12.9 cc of 32% " "
OR 12.0 cc of 35% " "

Add it to **2)** slowly with stirring; the yellow solution turns green.

4) & **5)** Continue with steps as in **A** above**.**

C. High Contrast: Exposure Scale ~1.8

1) & **2)** Follow these steps as in **A** above, then substitute the following for **3)**:

3) Use a measuring cylinder (US: "graduate"), or preferably a graduated pipette, to measure out:

44.0 cc of 10% *w/w* ammonia solution.
OR 19.3 cc of 24% *w/w* ammonia made up to 44 cc with water.
OR 18.5 cc of 25% " "
OR 16.8 cc of 28% " "
OR 15.7 cc of 30% " "
OR 14.8 cc of 32% " "
OR 13.7 cc of 35% " "

Add it to **2)** slowly with stirring; the yellow solution turns green.

4) & **5)** Continue with steps as in **A** above**.**

Intermediate degrees of contrast with Exposure Scales lying between 2.7 and 1.8 can be obtained by mixing sensitizer solutions A and C proportionally.

Preparation of 'Two-bottle' Sensitizers

Solution I Ammonium dicitratoferrate

A. Low Contrast: Exposure Scale ~2.7

1) Weigh out 13 g of citric acid monohydrate into a 200+ cc beaker.
OR 12 g of citric acid anhydrous.

Add 20 cc of pure water, warm (30ºC), and stir to dissolve the solid.

2) Weigh out 12 g of iron(III) nitrate nonahydrate. **Immediately** add the solid to solution **1)** a little at a time, stirring to dissolve it.

Cool the solution to room temperature before proceeding to **3)**.

3) Use a measuring cylinder, or preferably a graduated pipette, to measure out:

14.5 cc of 24% *w/w* ammonia
OR 13.9 cc of 25% **OR** 12.6 cc of 28% **OR** 11.8 cc of 30%
OR 11.1 cc of 32% **OR** 10.3 cc of 35%

Add it to **2)** slowly, dropwise, with efficient stirring.

4) Transfer solution **3)** to a measuring cylinder or volumetric flask and make it up with pure water to a final volume of 50 cc and mix well. Filter it if necessary. Transfer the solution to a well-stoppered brown glass bottle. Label and date it, and store in the dark.

B. Medium Contrast: ES ~2.3

1) & **2)** Follow the procedure as in A above.

3) Use a measuring cylinder, or preferably a graduated pipette, to measure out:

16.9 cc of 24% *w/w* ammonia
OR 16.2 cc of 25% **OR** 14.7 cc of 28% **OR** 13.8 cc of 30%
OR 12.9 cc of 32% **OR** 12.0 cc of 35%

Add it to **2)** slowly, dropwise, with efficient stirring.

4) Transfer solution **3)** to a measuring cylinder or volumetric flask and make it up with pure water to a final volume of 50 cc and mix well. Filter it if necessary. Transfer the solution to a well-stoppered brown glass bottle. Label and date it, and store in the dark.

C. High Contrast ES ~1.8

1) & **2)** Follow the procedure as in A above.

3) Use a measuring cylinder, or preferably a graduated pipette, to measure out:

19.3 cc of 24% *w/w* ammonia
OR 18.5 cc of 25% **OR** 16.8 cc of 28% **OR** 15.7 cc of 30%
OR 14.8 cc of 32% **OR** 13.7 cc of 35%

Add it to **2)** slowly, dropwise, with efficient stirring.

4) Transfer solution **3)** to a measuring cylinder or volumetric flask and make it up with pure water to a final volume of 50 cc and mix well. Filter it if necessary. Transfer the solution to a well-stoppered brown glass bottle. Label and date it, and store in the dark.

Solution II Potassium ferricyanide

5) Weigh out 10 g of potassium ferricyanide, purity 99%.
Add 40 cc of pure water and stir well to dissolve all the crystals. Make up with water in a measuring cylinder or volumetric flask to 50 cc. Mix well and transfer the solution to a well-stoppered brown glass bottle. Label and date it, and store in the dark.

To use 'Two-bottle' Sensitizers

Mix equal volumes of Solutions I & II to provide the working sensitizer solution - but only when needed.

The separate stock solutions I & II should keep indefinitely, but the mixed working sensitizer has an unpredictable shelf-life of only a few weeks, or even days, depending on the environment. Decomposition is signalled by a colour change from yellow to dark blue, due to precipitation of Prussian blue, which can cause blue speckles in the image. These may sometimes be avoided by filtering a working solution that has turned bad.

Equipment and Materials for Coating and Printing Cyanotypes

Paper: pure cellulose, unbuffered, internally sized with AKD

Glass coating rod or brush

Blotting strips

Syringes or pipettes, Calibrated 2 cc and 5 cc

Glass plate

Spirit level

Drafting tape or clips

Print frame

UVA light source

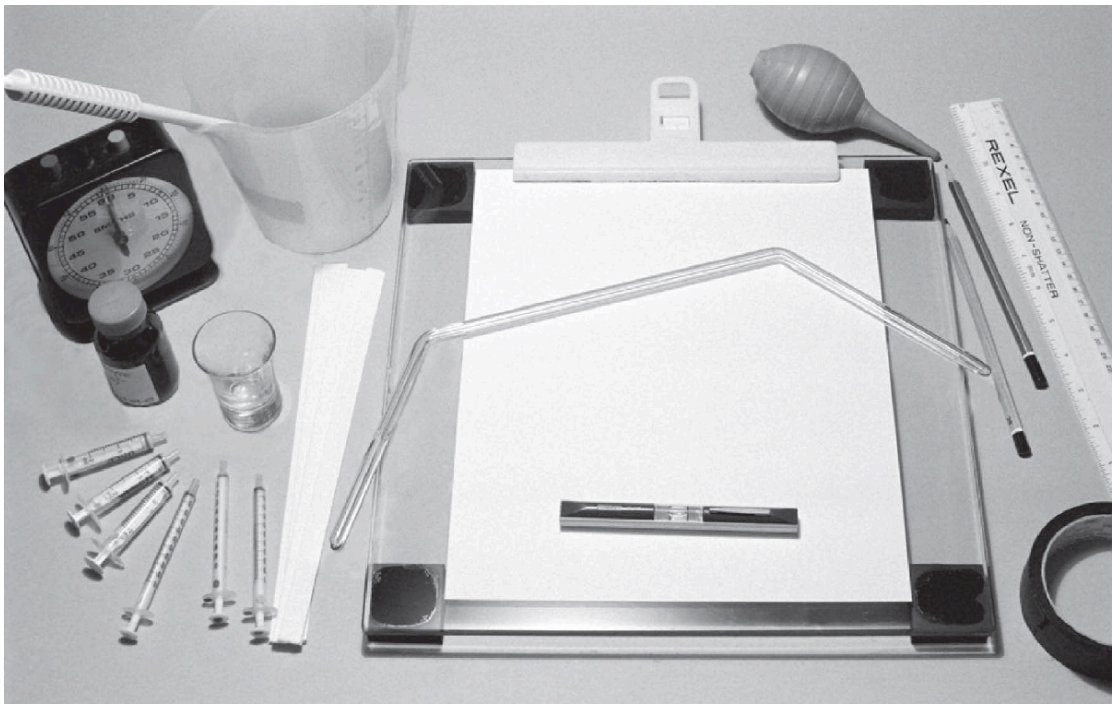
Timer

Plastic measuring jug 1–2 litre

Stirrer

Processing Dishes (2)

Drying line and pegs or drying screen



Illustrative of typical equipment – not all included here.

Procedure for the Simple 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:

- Arches Platine
- Bergger COT 320
- Legion Revere Platinum
- Hahnemühle Platinum Rag

If buffered papers are unavoidable, they should be pre-treated in a bath of dilute (5% *v/v*) hydrochloric acid, or 5-10% *w/v* sulphamic acid, to destroy the chalk, then washed. The use of oxalic acid is not recommended because calcium oxalate is as insoluble as calcium carbonate. 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 weight of 240 gsm, or more, will minimise "bellying" of the wetted area of the coated sheet, which will contact the negative better and be more robust in wet handling.

Negatives and Control of Contrast

Negatives may have a long density range (in the UV): as much as 2.7, to produce a full tonal range in a print made with the low contrast sensitizer A. This version particularly commends itself for preparing digital negatives by the PiezoDN protocols. By making use of the variable contrast adjustment, sensitizers may be formulated to match their Exposure Scale to the density range of silver-gelatin negatives prepared for other processes, such as platinotype or palladiotype.

Addition of Surfactant to the Sensitizer

The success of cyanotype depends on the sensitizer penetrating the interfibrillar space of the surface cellulose fibres, where the pigment will be trapped, and not simply remaining in the coarse pores of the paper, from which it washes out. To assist retention and to provide a more uniformly coated surface, a surfactant (or 'wetting agent') is used. Tween 20™ (a non-ionic surfactant) is added to the sensitizer solution just before coating to produce a final concentration of *ca.* 0.25-0.5%. *i.e.* one drop (*ca.* 0.05 cc) of a 15% *v/v* stock solution of Tween 20™ is added to each 3 cc of sensitizer and mixed in well. For larger coating volumes, add one drop of a 25% *v/v* stock solution of Tween 20™ to each 5 cc of sensitizer. Do not use Tween 80™ which causes foam. Do not add Tween to the stock sensitizer solution: it doesn't last very well when dilute, and the appropriate amount - to be found by trial - will depend upon the chosen paper.

Coating

Coating by the rod method (*ca.* 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. For instructions see:

http://www.mikeware.co.uk/mikeware/preparations.html
https://www.dropbox.com/s/yf6z1kftk7q2xcf/coating.mov?dl=0

Drying

Let the sensitized paper dry at room temperature in the dark for an hour or two. Shorter drying times are possible, but very humid paper may damage silver-gelatin negatives, and not lie flat due to swelling.

Alternatively, allow a few minutes for the sensitizer to soak in, until the paper surface appears non-reflective, then heat-dry it with a uniform air stream at *ca.* 40°C for *ca.* 5 minutes. Heat drying of a cyanotype paper appears to increase the contrast slightly (~1 stop). Prompt drying can diminish any chemical fogging due to impurities in the paper; but note that over-rapid drying may diminish penetration of the sensitizer and 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, worse, blue, the highlights are chemically fogged, so reject it and find a better paper.

Printing Exposure

Exposure depends on the chosen scale of contrast but is significantly shorter than that needed for the Classic cyanotype process - probably about 5 to 10 minutes under an average 365 nm UVA light source (e.g. a facial tanning unit) should suffice.

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 light green, the mid-tones are firm blue, and the deepest shadow tones are reversed to a pale blue-grey, giving the image a 'solarised' look. If the print is left in the dark for some hours *before* wet processing, another stop of highlight detail may become apparent.

The coated paper sheet in the printing frame should be backed with a sheet of papermakers' felt, or other porous material, to provide a passage for the carbon dioxide gas evolved during the exposure. Otherwise, acutance may be lost due to bubbles of gas forming between negative and paper surface.

Wet Processing

1 Develop in 1% citric acid for half to one minute with agitation – until Prussian blue starts to runoff, then transfer to the water wash. If high-lights appear to be unduly blued, use citric acid more dilute than 1%. Omitting this acidic bath and simply processing in water produces a much shorter Exposure Scale of ~1.3, with higher contrast and no fogging but a somewhat weakened D_{max}.

2 Water Wash: immerse face down in gently running water for ~10 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 or four baths of static water may be used.

The reversed shadow tones regain density fairly rapidly by air reoxidation during wet processing and drying, but if completion of the regain is required immediately –e.g. for densitometry– then 50 cc of 6% hydrogen peroxide ("20 Volume") may be added per litre of the first wash bath. Blued highlights may be cleared by immersion in a 1% bath of ammonium oxalate for a few minutes.

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 daylight (2000 lux) or bright gallery illumination, but this loss is regained on dark storage in the air, and their full density should return after a few days. Exhibition under low light levels (50 to 200 lux) should cause no measurable fading. For conservation information see:

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

Summary of Simple Cyanotype Procedure

1. **Unbuffered paper:** choose side, mark up coating area

2. **Syringe out sensitizer:** add Tween to final strength ~0.25–0.5 %

3. **Rod Coat:** ~1.5 cc per 10 x 8 in. area: 5–8 'passes' of coating rod

4. **Dry in dark:** 1–2 hours at room temp, or 40°C air for 10 minutes

5. **Negative**: density range from 1.8 to a maximum 2.8, in the UVA

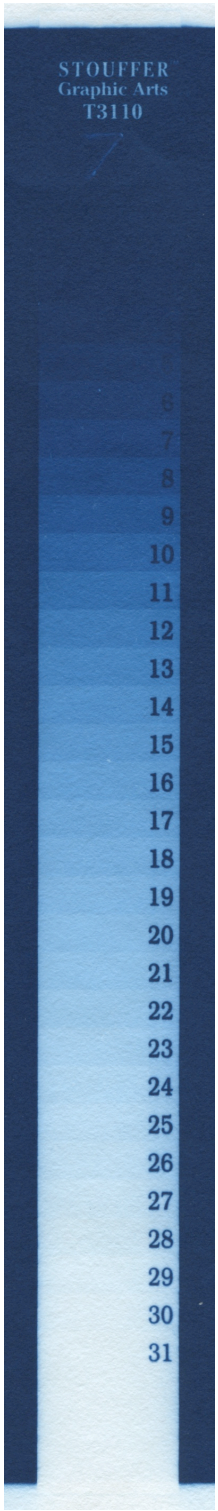
6. **Expose to UVA:** until high values green and deep shadows reversed

7. **Develop:** ½ minute in ~1% citric acid; or water for more contrast

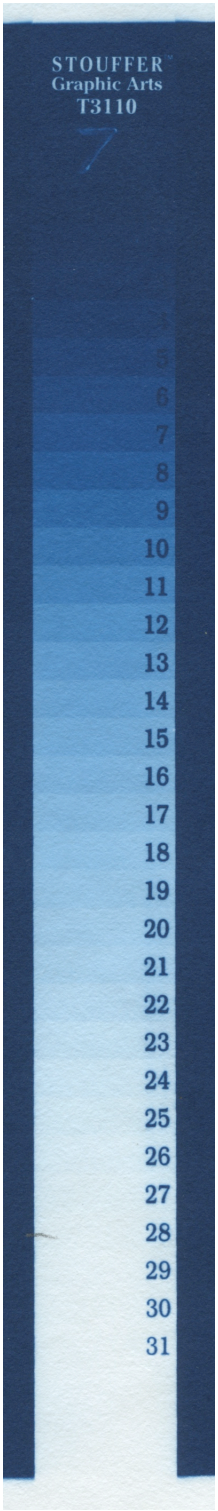
8. **Wash:** in non-alkaline, non-hard water for 10 minutes

Typical results for Simple Cyanotype: One-bottle version

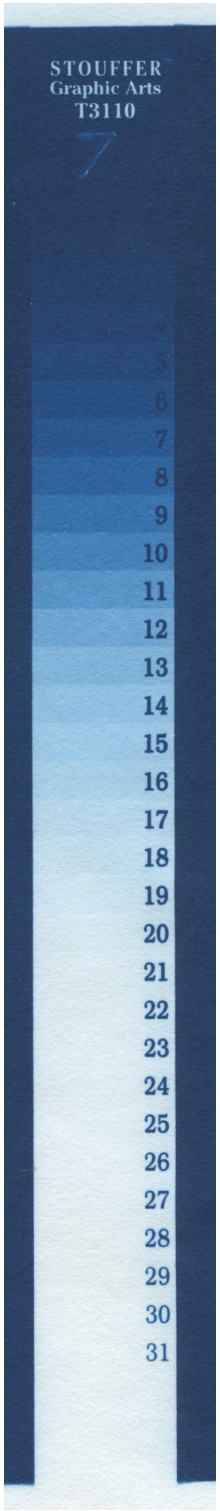
Three contrast grades A, B, C. Sensitizer pH given.
Buxton paper 160 gsm. Tween 0.3%. 8½ minute exposure facial unit
A, B, C Developed in 1% citric acid for ½ minute. D in water only.



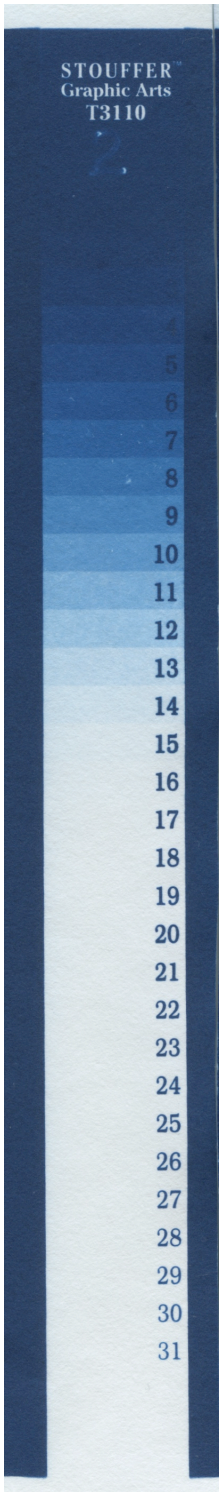
A. ES ~ 2.7
pH ~ 4



B. ES ~ 2.3
pH ~ 6



C. ES ~ 1.8
pH ~ 8



D. ES ~ 1.3
Water developed