# Introducing Blythtypes: Positive-working Cyanotype prints!

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# Abstract

This paper describes a new Cyanotype system, *the ‘Blythtype’*, which offers a new technique resulting in a positive image made from a positive image. Another advantage of this new technique is the increase in light sensitivity through the introduction of a photosensitive dye. Crucially, it also offers photosensitivity to the red end of the spectrum enabling a greater balance of grey scales to be recorded from coloured images which until now has not been directly possible with Cyanotypes. The authors hope this will excite many home based Cyanotype experimenters to have a go. Some chemical mechanics of how this new system is thought to work is given at the end.

This new ‘*positive-working- Cyanotype system*’ has three great advantages.

1. It does not need a negative image sheet.
2. It allows a modern digital projector to be used, as one might a photographic enlarger.
3. It allows old transparencies like ‘Kodachromes’ to be turned directly into cyanotype images using old analogue projectors.

*(All chemicals and equipment are readily available at low cost from Internet suppliers. Without exception the chemicals advocated are not acutely toxic, nevertheless safety precautions should always be taken to keep chemicals away from children).*

# *Key Words: Cyanotype, Blythtype, Positive-working, Photographic Blueprint, Prussian Blue.*

**Our Procedure**

1. Coat a specific brand of semi-gloss photo-paper with a solution of the dye thionin acetate.
2. To then readily convert that thionin acetate coating into the less soluble salt thionin ferricyanide.
3. To then coat the sheet with a special photosensitizing liquid we have developed.
4. To then expose the covered sheet to the image from a projector.
5. To then develop the exposed sheet in acidic ferrous sulphate solution where it creates the famous Prussian Blue pigment and removes thionin dye.

**Chemicals Required**

* De-ionized or distilled water (DI) . (One can just use the water collected from say a domestic tumble drier).
* Potassium ferricyanide (available from [www.magnacol.co.uk](http://www.magnacol.co.uk) or in USA and Canada from <http://www.artcraftchemicals.com> )
* Thionin dye, the chloride salt is the most preferable and was until recent years the standard form of it. But the acetate salt is now the only form commonly available (eg. from [www.magnacol.co.uk](http://www.magnacol.co.uk) ) . [A special offer of thionin is available for a limited period in the USA and Canada from <http://www.artcraftchemicals.com> ]
* Ferrous sulphate (sulfate). Available in USA and Canada from <http://www.artcraftchemicals.com>
* Sodium bisulphate (sodium hydrogen sulphate). N.B. Not “bisulphite”.
* EDTA (ethylenediaminetetraacetic acid, the free acid powder) . [N.B. **This MUST be the free acid powder and not a sodium salt**]. (Available from [www.magnacol.co.uk](http://www.magnacol.co.uk) ). For USA, or Canada, <https://apcpure.com>
* Sodium sulphite (sulfite) anhydrous. Na2SO3. . Available in USA and Canada from <http://www.artcraftchemicals.com>

DEA, Diethanolamine. (Available from [www.magnacol.co.uk](http://www.magnacol.co.uk) ). Alternatively **TRIS Base** can be used. This is a convenient solid crystalline alternative which gives the same result as DEA but needs about double the exposure time. Available from :

<https://www.ebay.com/itm/Tris-Base-Ultrapure-for-Laboratory-Use-100g-25kg/162627543198?hash=item25dd5b609e:m:mZuXSBocNPGyvCdoXMNjwWw>

**Materials for making the photosensitive sheets**

Through extensive testing we have found so far only two inkjet photo printing papers that are suitable for this process., We think it is essential to start with one of these two brands. The problem with many inkjet photopaper brands tested, both full-gloss and matt, or indeed any ordinary printing paper, seems to be that the dye penetrates too deeply into the fibres and backing and this inhibits the dye’s vital photobleaching reaction. The backside of both these products are waterproof, and essentially the dye will not penetrate into them.

Check list of required items:

* Epson PREMIUM SEMIGLOSS photo paper [251 gsm] A4. Epson also offer a size 14% larger than A3. Alternatively, Jessops A4“SATIN” photo paper [240gsm]. A3 size is also available.
* One weighing machine capable of weighing to 0.10g
* A good quality soft squeegee. e.g. GB Pro 14”. (This will work also on A3 size.)
* A calibrated beaker, or jug, that will hold more than a litre.
* Two small soft sponges of different colours.
* Surgical gloves
* To prepare A4 sized sheets we use a 3mm thick piece of PMMA sheet also known as “Perspex”, “Plexiglass” or just “acrylic”. We call this the “carrier sheet”. we use about a 5 cm border all around when an A4 photosheetisplaced in the centre. (A3 sized sheets will of course require an A3 sized sheet plus an extra border). This sheet does not have to be transparent, but it should not be white as that will cause back-scatter when it is supporting a sheet of film in the projector beam. A glass sheet is also good but less user-friendly and as it has to be handled a lot, the sharp edges and corners should be smoothed off.
* **A4 trays for processing baths**

We use very low-cost plastic “Kitty Litter” trays . The coating procedure should be kept quite separate from the later photosensitizing procedure which is done just before the exposure and development procedure. So one can use the same trays after carefully washing them free of the chemicals used in the initial coating procedure. We use 2 trays to hold 2 solutions for initially coating sheets, and then we dry the sheets well. Later we need 1 tray to make the sheet photosensitive and one tray to hold developer after the exposure and 1 tray to hold a final treatment after development. This last tray ideally needs an extra tray to act as a floating lid on about 1 litre of liquid to minimise oxygen absorption. A minimum of about 250ml of liquid is needed for a bath so that it completely covers the smooth floor of an A4 tray. For A3 sized sheets we use polypropylene storage trays.

**Thionine dye bath**.

For the Epson “Semigloss” photopaper, we add 1.0g thionine acetate (or chloride) to a clean 1 litre beaker , then we add 260 ml of hot (~70 oC) de-ionized or distilled water (DI) This is then stirred for about 15 minutes.. For the Jessops Satin photopaper we start with 1.3g of thionine dye and then we add 260 ml of hot (~70 oC) de-ionized or distilled water (DI) This is then stirred for about 15 minutes. The thionin solution is then left to cool for several hours before use. During this time, thionin forms peculiar aggregations of molecules such as dimers and trimers [ 1 ] so that one can later get richer dye coatings from cold solutions than hot ones. Once in a tray the cold solution can be used indefinitely but needs to be stored in a bottle to stop water evaporation. We have recently been surprised to find that coating works best without the addition of alcohol, or a surfactant. (In contrast to our previous recipe).

**Potassium ferricyanide bath**.

About 150g of potassium ferricyanide is stirred into 1 litre of DI in a jug or beaker until dissolved. In a tray, it can be used indefinitely, but should be stored in a bottle to prevent too much water evaporating.

**The Photosensitizing bath. Either using DEA or the TRIS BASE alternative**

100.0g (**not ml**.) diethanolamine (DEA), is stirred into 200 ml. of DI and stirred to form a clear solution (soln.) in a glass or plastic beaker or jug. Then 91g of EDTA powder (N.B. **NOT** **the sodium salt form of EDTA)** is poured in and stirred continuously until a completely clear solution results. The clear solution may warm up to about 35o C during this neutralization step. This quantity of liquid is sufficient to cover the floor of one of our A4 trays. (The pH finishes up at around 7 when it has cooled down to about 20 oC.). This concentrated solution keeps well and can be used many times, it just needs protection from evaporation in the long term.

If TRIS Base is being used instead of DEA, The same method is used as for DEA but the ratios differ to get to a neutral pH.

120g TRIS Base is stirred into 200ml of warm DI (~50 oC.) and then 100g EDTA (**Not** the sodium salt) is stirred in for as long as it takes to get a clear solution. (The pH finishes up at around 7 when it has cooled down to about 20 oC.).

**Ferrous sulphate developer bath**

We stir in 20g. sodium bisulphate to a litre of water in a beaker or jug (tap-water is quite OK here, cold or warm from the hot tap is better than using cold water from the cold tap as it will contain less oxygen). Then about 15g. of ferrous sulphate is stirred in. This is then poured into a tray. This acidic solution slowly absorbs oxygen. It works well to use another tray as a floating lid when the soln. is not in use, it can then last for days..

**Sulphite bath. (The final bath).**

About 30g. anhydrous sodium sulphite (Na2SO3) is stirred into 1 litre tap water in a beaker or jug. This somewhat alkaline solution will absorb oxygen more rapidly than the previous soln. when it is in an open tray. It works well to use another tray as a floating lid when the solution is not in use .

**Method**

1. Under ordinary room lighting, the thionin soln. is put in a tray. The photopaper sheet is now going to be placed upside down on the surface of the thionin dye soln. A good technique here is to place the sheet on the surface with both hands so that the front of the sheet is somewhat convex so that the middle of the sheet first touches the liquid in the centre of the tray and the sheet is then allowed to flatten out and push any surface bubbles away. It is then left to float flat on the surface for about 2 minutes (we have not found that it matters if it is 10 minutes). It does not matter much if the dye also gets on the back of the sheet, but it makes the squeegeeing procedure easier and wastes less dye if the amount on the back is minimal. The sheet is then lifted off the surface by holding just a corner and liquid is allowed to drip off the opposite corner for about 30 seconds before being placed face up on a clean flat very smooth surface such as the acrylic “carrier sheet”.
2. A “handling edge” is chosen which will not be in the final image area. The handling edge is held firmly down using the gloved thumb and index finger spread as widely as possible so that the sheet will not slip, the squeegee is then pulled down the coated sheet fairly carefully and evenly with a firm downward pressure so that the excess dye is swept off the other end of the sheet. This excess dye can be squeegeed into a folded strip of water-proof film when one edge is tucked under the carrier sheet. The excess dye can then be poured back into the bath. (The back of a discarded wide strip of the type of photopaper being used here works fine for this).
3. The coated sheet should now look homogenous (except for the handling edge).

Each coated sheet must be completely dry before the next step to photosensitize it. We find it best to use warm air from a hairdryer clamped about 1 metre above the sheet which is resting below on paper towelling.

1. Under ordinary room lighting, the dried thionin coated sheet is then totally immersed face up in the bath of potassium ferricyanide solution, where it is gently rocked for about a minute, and then left for another minute. (No difference has been detected if it is left in this bath for 20 minutes). This step is transforming the thionine acetate coating into a much less soluble thionin ferricyanide coating. The sheet must then be washed entirely free of the very soluble potassium ferricyanide soln. We do this by using a good flow of cold tap water, first rinsing the yellow solution off the back of the sheet and then using a soft sponge to help fully remove all traces of solution off the front. The tap water is now squeegeed off the sheet before it is dried again under a warm but not hot air flow.
2. The photosensitization step must now be carried out under dim lighting. The dried coated sheet is placed upside down in the photosensitizing solution. As before, a good technique here is to place the sheet on the surface with both hands so that the front of the sheet is somewhat convex so that the middle of the sheet first touches the liquid in the middle of the tray and is then allowed to flatten out and push any surface bubbles away. It is then left to float flat on the surface for about a minute. It is then lifted out and held by a corner so that excess liquid streams and drips off into the bath before being placed face up on the carrier sheet. A few drips of this concentrated liquid on the back of the coated sheet serves to effectively hold the photosheet in place by capillary action after the squeegee is used. The sheet is held down firmly along the handling edge using a widely spaced thumb and index finger and the excess liquid is removed with a firm swipe of the squeegee. This excess concentrated sensitizer is not wasted . It can be squeegeed onto a wide folded strip of water-proof film when one edge is tucked under the carrier sheet. The excess liquid can then be poured back into the bath. (The back of a discarded wide strip of the type of photopaper being used here works fine for this).
3. The carrier sheet and coated photosheet are now ready to be positioned in front of the projector set-up. This needs to have been pre-arranged so that it will all be in perfect focus when the carrier sheet is put in a marked out vertical position. It is now important to keep in mind that using a projector as a photographic enlarger creates a strict requirement that you never have to consider normally when using a screen. This is that during the exposure period, there must be not the slightest movement or displacement between the photosheet and the projector, or the image will finish up blurred. The projected light is blocked off with something that can act as a shutter that can be lifted off or slid sideways. If you initially need to adjust the exact position of the photosheet then it should be done in less than 5 seconds from the start of the exposure. ( We have found it particularly useful to use a piece of high optical density sheet as a shutter so that we could adjust the position of the very dimmed down image exactly where we want it on the photosheet).
4. To judge if there has been enough exposure after a period, we completely block the projector light briefly and examine the sheet under non-bright torch-light. If just the brightest highlights in the image can be faintly seen, then the exposure is probably enough. If on the other hand the whole picture can be seen, then it is probable that it is overexposed. With regard to the image size being projected, our latest findings are for example that if DEA/EDTA was used as the sensitizer then an A5 sized bright image might need less than a 1 minute exposure, an A4 about 2 minutes, and an A3 about 4 minutes, but if the photosensitizer used was the TRIS/EDTA then these exposure times needed to be doubled. But all this can of course vary greatly depending on picture and projector.
5. Under dim lighting, the exposed sheet now needs to be briskly washed entirely free of the sensitizing solution or it will not form that vital Prussian Blue (PB) pigment in the acidic ferrous sulphate developer bath. This sink washing process is carried out using a good flow of cold tap-water while gently rubbing all over the sheet with a soft sponge, (preferably a different sponge from the one that was used to prepare the sheet earlier), this procedure should preferably take less than a minute, and should include a brief rinse of the back of the sheet.
6. **The developing bath:** The washed sheet is then quickly placed in the acidic ferrous sulphate bath (so that the whole sheet gets simultaneously covered). Bright lighting is OK now. The bath then needs to be rocked for at least a minute., Although the image usually shows up strongly in about 10 seconds, it is necessary to continue agitating the sheet for at least a minute so that the thionin dye can be solubilised and removed (unless you would like a violet print). It is then briefly rinsed , front and back, under running tap water and then immersed in the final bath of sodium sulphite solution and well agitated for about half a minute. It is then rinsed under running tap water, front and back to remove the sulphite soln. The water on the surface is then squeegeed off with a clean squeegee and the sheet is dried in a warm air flow.

**Manipulation of contrast**

There is much discussion of ways to increase or decrease contrast in traditionally made Cyanotypes in refs [2][3][4] Some of these ways may also work on the Blythtype.

**Discussion of possible chemical mechanisms**

* The coated thionin dye in the form of its acetate or chloride salt is readily converted to a less soluble salt by immersing it in concentrated potassium ferricyanide solution. The resulting thionin ferricyanide coating is then made light sensitive by coating it with the concentrated solution of diethanolamine EDTA salt.

The relatively viscous and concentrated photosensitizing layer on the photosheet needs to be squeeged off after a minute for two reasons.

1) A thick layer causes dye to dissolve into it and this can act as an uneven light filter.

2) A thick layer has a lensing effect which slightly defocusses the image.

However, if the sensitizing solution is made more dilute and less viscous in the first place, it reduces its photosensitizing ability very substantially. The pH is neutral and the solution is not harmful if it accidentally gets on unbroken skin. It is very water soluble.

It is thought that in the imaging process, light causes the dyed photosheet to bleach and momentarily to produce a colourless compound known as leuco-thionin. This reduced form of the dye then seeks to return to its non-reduced coloured form by reducing its ionically attached ferricyanide anion to form thionin ferrocyanide. The proportion of ferricyanide ion converted to ferrocyanide ion is dependent on the light intensity on that area and also of course, the exposure time. In the highlight areas of the image, the conversion to ferrocyanide can approach 100% and in the darkest areas the conversion can be almost zero. When the exposed sheet is immersed in the acidic ferrous sulphate solution, the famous Prussian Blue (PB) pigment forms only where thionin ferricyanide still exists, and this allows the thionin dye to get washed into solution as a sulphate salt. But PB does not form when it meets thionine ferrocyanide in the light-struck areas, (which makes this a positive-working system). Therefore in the highlight areas very little Prussian Blue is formed and it may be predominantly “Prussian White” or “Williamson’s White” (WW) and this is a form of an insoluble ferrous ferrocyanide salt. [ref.2, p293]. WW formation also allows the thionin to form a sulphate salt. However this WW salt can quite rapidly absorb oxygen when wet , or even apparently dry and this then forms PB and can start to create a blue veil over the image, particularly in the highlight areas. We have spent some time working on how to deal with this effect easily and cheaply. We were pleased to discover that a final bath of sodium sulphite stops the “blueing” effect permanently. Its effectiveness is not simply caused by a chemical reduction process, because more powerful reducing agents such as sodium bisulphite do not work.

We made the important discovery some years ago that neutralizing EDTA with certain amines had a strong synergistic effect when it came to photobleaching the dye methylene blue (tetramethyl thionin) . After testing a number of aliphatic amines for our new discovery, the best amine found that worked, and was also not volatile, smelly or inflammable and could be bought on line by home users was diethanolamine. We had originally been disappointed to find that triethanolamine and other tertiary aliphatic amines which had long been known to photobleach MB [5][6] ]did not work well in our system, but thanks to an inspired suggestion from Alan Meredith-Jones of Magnacol Ltd, we found that diethanolamine worked very well indeed, much to our amazement, because it was a secondary amine. He also suggested trying the primary amine “TRIS Base” tris(hydroxymethyl)aminomethane which is a very convenient crystalline powder commonly used in biotechnology. Astonishingly, this one also worked although the exposure times needed were twice as long, this was still very good and a viable alternative to liquid DEA.

Unfortunately the cheaper methylene blue (MB) dye failed to work in this Blythtype method. It appeared to be due to the colourless leuco MB ferricyanide failing to form the sufficiently stable ferrocyanide salt that was hoped for. But that then led us to the important discovery that unlike MB, thionin did actually work as was hoped.

**REFERENCES**

## Lai, W.C. Dixit, N.S. Mackay, R.A. Formation of H Aggregates of Thionine Dye in water. *J. Phys. Chem*. 1984, 88, 5364-8

## https://www.mikeware.co.uk/downloads/Cyanomicon\_II.pdf

## James, C., The Book of Alternative Photographic Processes, 3rd Edition, pub. Cengage Learning 2016. ISBN: 978-1-285-08931-7

## Mrhar, P., [www.petermrhar.com/alternative](http://www.petermrhar.com/alternative)

## Kayser, R.,Young, R., The photoreduction of methylene blue by amines. *Photochem. Photobiol.* 1976, 24, 395

## Oster, G., Wotherspoon, N., Photoreduction of methylene blue by ethylenediaminetetra acetic acid. *J.Am.Chem. Soc*. 1957, 79, 4836.