

Introduction

Since the beginnings of civilisation, human beings have had an urge to create art, and for as long as they have had this urge, they have harnessed science in its assistance. From Neolithic man's utilising the pyrolysis of wood to create charcoal for his cave paintings to the myriad of synthetic pigments available to the artists of today, science, in particular chemistry, has been an indispensable assistant.

In no field has this been more the case than that of photography; an art form that has had enormous impact on our civilisation. Our record of the late 19th century is much richer and more complete than that of the early 19th century, in part because of the use of photographs to document historic events, places and people.

History of photography

The story of photography really begins with the camera obscura (ca. 1580 AD). This was a dark room with a lens mounted in one wall which projected a scene onto the opposite wall. An artist could sit in the room and trace the image to produce a very accurate record of the scene. You might want to take a trip to the one in Edinburgh [1], next to Edinburgh Castle. Rather than concentrating on the optics of producing a temporary image, here we look at the development (sorry!) of the chemistry involved in making these images longer lasting.

Beaudelaire described photography as a 'bastard child left by chemistry on the doorstep of art'. A bit harsh, perhaps but he has a point. The conception of this child was probably in 1725 when Johann Schulze discovered that silver nitrate was light sensitive. A sheet of paper soaked in silver nitrate would turn black wherever light hit it as silver ions were reduced to silver metal. The image was not fixed, however, in the sense that when the photograph was brought into daylight, the whole image would turn black.

It took a gestation of almost 100 years though for the prodigal child to come to term. In 1819 William Herschel discovered that sodium thiosulphate (known then as hyposulphite, hence the photographer's term 'hypo') was found to remove the unexposed silver halides, leaving a permanent or "fixed" image behind.

The first photographic process was invented by Joseph Niépce around 1822, which he used to make the earliest known permanent photograph. The process, called Heliography, used bitumen, as a coating on glass or metal, which hardened in relation to exposure to light. When the plate was washed with oil of lavender, only the hardened image area remained. (Figure 1).

The first widely used photographic processes were developed independently in England and France and both used silver compounds. In 1834, Henry Fox



Figure 1 - The first successful permanent photograph. View from the window at Le Gras (1826)
http://en.wikipedia.org/wiki/View_from_the_window_at_Le_Gras

Talbot created permanent (negative) images using paper soaked in silver chloride and fixed with a salt solution. He then created positive images by contact printing onto another sheet of paper. In 1837, Louis Daguerre created images on silver-plated copper, coated with silver iodide and "developed" with warmed mercury. The Daguerrotype was initially more popular but soon the ability of Fox Talbot's negative process to allow production of numerous prints from a single negative made it the dominant process and the basis for all photography until the rise of modern digital imaging.

Silver processes were improved continuously throughout the 19th and early 20th centuries. Silver bromide replaced the earlier silver chloride and iodide processes beginning in 1885. Today almost all photographic film consists of silver bromide on acetate film. Almost all photographic paper is silver bromide on various papers.

Alternative processes

As we have discussed, most photography is based on silver salts as the light-sensitive agent. For the classroom, however, these processes have a few drawbacks, not the least of which is the cost of the silver-based reagents. There are, however, several non-silver processes that were developed in the early days of photography and it is these that are of more interest to the chemist-photographer.



John Heinrich Schulze.

William Herschel.

John Heinrich Schulze.

Platinotypes are based on platinum chloride – hardly a cost-cutting reagent! Gum bichromate is a process growing in popularity but it uses dichromates, which are on SSERC's restricted chemicals list and are not generally recommended for use in schools, so we'll leave that alone. Cyanotype and Anthotype processes, though, are more promising, using respectively light-sensitive iron and botanical compounds.

Cyanotypes

This was yet another process invented by William Herschel, also in 1842. It uses iron salts to create a blue pigment – Prussian blue. The blue colour was its weakness from the point of view of popularity with the public but the images were stable, clear and easy to make and proved a big hit in the reproduction of architectural drawings – hence the word 'blueprint'.

There has been a renewed interest in this process over recent years and there are dozens of different recipes. Most of them



Figure 2 - A cyanotype image showing brush stroke and shadows of the paper clips that held it in place.



Figure 2 - A cyanotype image showing brush stroke and shadows of the paper clips that held it in place.

Fisch's ferro-prussiate

Advantages

Easy to do and relatively cheap. Images are stable

Disadvantages

Images have a pronounced blue cast

(though they can be easily stained by e.g. tea)

Method

1. Dissolve 145.5 g of iron(III) (ferric) chloride in 100 cm³ of water. (This is close to being a saturated solution so will take some dissolving)
2. Weigh 25 g of 2,3-dihydroxybutanedioic acid (tartaric acid) and dissolve in 100 cm³ of water
3. Mix solutions 1. and 2.
4. Add up to 47 cm³ ammonia (0.880), stirring constantly, until neutral – Health & Safety data from Hazardous Chemicals [2]
5. Label this Solution A.
6. Weigh 20 g of potassium hexacyanoferrate(III)-3-water (ferricyanide) neutral – Health & Safety data from Hazardous Chemicals [3] and dissolve in 72 cm³ of water.
7. Label this Solution B.
8. Add all of solution B to solution A with constant stirring.
9. When it is cool, pour into a dark bottle and store in the dark until use.
10. This should give about 275 cm³ – enough for around 50 A4 sized sheets – depending on paper.
11. Use a brush or sponge to coat your paper and allow to dry in the dark.
12. Sandwich your negative against the paper (hold in place with a clip frame – or even Sellotape@!)
13. Place the picture in direct sunlight for about 15 minutes (some experimentation will be needed)*
14. Remove and wash the paper in cold running water until all the yellow, unreacted salts are gone. Allow to dry.
15. If you want to speed it up, expose for a much shorter time (2-3) minutes and soak in vinegar (distilled malt vinegar) before washing)

are based on iron(III) ammonium citrate though the newer ones use iron(III) ammonium oxalate. These are not chemicals commonly found in a school chemistry store and, while less expensive than silver salts, they are not especially cheap to obtain.

There is, however, an alternative – Fisch's ferro-prussiate – which we have been testing with some degree of success.

Anthotypes

This long neglected process, originally invented by Sir William Herschel in 1842, is extremely simple. An emulsion is made from crushed flower petals or any other light-sensitive plant, fruit or vegetable. A coated sheet of paper is then dried, exposed to direct full sun-light until the image is bleached out. The process does have a couple of disadvantages (see p8).

Negatives

Thanks to modern technology, negatives are now quite easy to produce. Take any image you like and use a photo editing

program to convert it to black and white and then invert the colours. This can then be printed onto acetate film by an ordinary printer found in any school.

If you don't have access to bespoke software such as Adobe's Photoshop, there is a free program called Paint.Net available online which will do all sorts of things for you – including making negatives.

Or you can simply get pupils to draw patterns on an acetate sheet using felt pens (or even a polythene document sleeve) and use those as negatives - or even cut out silhouettes from paper.

Paper

The choice of paper seems to be quite critical for the Gum bichromate and Cyanotype processes. Ordinary A4 will not work! The cheapest viable option seems to be watercolour paper: available fairly inexpensively from many suppliers – or talk nicely to your school's art department.

Anthotypes**Advantages**

very easy, very cheap

Disadvantages

It is rather slow (exposure typically takes 1-3 days or more depending on conditions). The images fade when exposed to bright light

Method

1. Take a flower (Research is still ongoing. Red roses work but very slowly. According to alternativephotography.com, red poppies or peonies work well, as do the leaves of laurel, common cabbage and some grasses)
2. Crush the plant material to a fine pulp in a pestle and mortar adding distilled water (or alcohol) as you go.
3. Filter the liquid.
4. Coat a sheet of paper with your emulsion and let it dry in the dark
5. Contact print your picture. A clip frame is an easy, cheap way to keep your negative in place. – or you can simply use Sellotape®.

By exploring radiations beyond the visible, I can describe a selected application, discussing the advantages and limitations.

SCN 3-11b

I have collaborated in activities which safely demonstrate simple chemical reactions using everyday chemicals. I can show an appreciation of a chemical reaction as being a change in which different materials are made. **SCN 2-19a**

Through experimentation, I can identify indicators of chemical reactions having occurred. I can describe ways of controlling the rate of reactions and can relate my findings to the world around me. **SCN 3-19a**

I have collaborated with others to find and present information on how scientists from Scotland and beyond have contributed to innovative research and development. **SCN 3-20a**

Higher

These reactions could slot into Unit one of the higher, either in part i) Following the course of a reaction or more specifically in part ii) Factors affecting the rate of a reaction where it is specifically recommended to demonstrate a photochemical reaction

Cross-Curricular links

Art: as a form of photography, there are obvious links e.g.

I have experimented with a range of media and technologies to create images and objects, using my understanding of their properties. **EXA 3-02a**

Technology: as well as obvious links with ICT in the production of negatives there may well be opportunities for further links – making the paper that the prints are made on for instance.

Conclusion

Here at SSERC we have only recently started looking again at these interesting and largely neglected processes. The cyanotype in particular seems to have some interesting possibilities, as well as some interesting chemistry, so you can look forward to something more on this at some stage in the near future.

Light

Most research has been done on the Cyanotype process. The peak sensitivity of the reagents in this process is in the near ultraviolet (UV) (around 475 nm). Sunlight is a convenient source of UV (indeed, daylight on a cloudy day will work too, albeit with longer exposure times).

The Gum bichromate process is also UV sensitive. As for the anthotypes, we have yet to determine but it would seem likely that it will vary depending on the particular pigment.

Educational value

1. This provides an opportunity to demonstrate, in an entertaining way, a photochemical reaction.

2. As these processes are relatively slow – the cyanotype reacts over a few minutes – it can provide a method for looking at reaction rates of a photochemical reaction

3. Because the cyanotype process works with UV light, it provided a method of investigating UV exposure or sunscreens. (Take an acetate sheet, put stripes of different sunscreens or different dilutions of sunscreen on and expose).

Links to Curriculum for Excellence (CfE)

By exploring reflections, the formation of shadows and the mixing of coloured lights, I can use my knowledge of the properties of light to show how it can be used in a creative way. **SCN 2-11b**

References and resources

[1] <http://www.camera-obscura.co.uk/>

[2] <http://tinyurl.com/HazChem-ammonia>

[3] <http://tinyurl.com/HazChem-Kferricyanide>

Alternative photography.com – as the name suggests, a website dedicated to renewing and refining all sorts of old, forgotten photographic processes.

<http://www.alternativephotography.com/wp/>

Project Vedos – a project carried out at Satakunta University of Applied Sciences / Fine Art, Kankaanpää, Finland. Its main goal is to study and teach alternative printing processes in photography and printmaking. <http://193.166.40.90/>

Cyanotype: Mike Ware Alternative Photography – Dr Ware is the undoubted expert in the chemistry of this long-neglected process. Most research will lead back to him eventually so take a short cut.

<http://www.mikeware.demon.co.uk/index.html#anchor930646>

Anthotype

<http://www.apug.org/forums/forum42/42719-anthotype-questions.html>

<http://photo.net/black-and-white-photo-film-processing-forum/00ILXh>

Gum Bichromate (plus a load of other interesting projects)

<http://cavemanchemistry.com/oldcave/projects/photo/index.html>