FERRIC and HELIOGRAPHIC PROCESSES

George E. Brown

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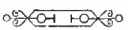
Ferric & Heliographic Processes:

A Handbook for Photographers, Draughtsmen, and Sun Printers

BY

GEORGE E. BROWN, F.I.C.

(Late of the G. W. Railway Co. Chemical Staff)



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INTRODUCTION

THIS little handbook is intended to serve two classes of people. First, amateur photographers, with a taste for experiment, who may find in the preparation of their own sensitive papers much interesting work; and, secondly, draughtsmen, engineers, architects, surveyors, and others, who find the reproduction of tracings and drawings a matter of every-day necessity.

It would have been easy to have made the manual greatly exceed its present proportions; but the writer has preferred to omit any notice of those processes, the difficulty or unreliability of which only makes their employment disappointing. Much, too, that might have been said on theoretical matters is omitted, the aim of the book being to be strictly practical.

Mr W. E. Brewerton has kindly supplied particulars of the process described in Chapter IV. The editor of the *International Annual of Anthony's Photographic Bulletin* has permitted the reproduction of figures 1, 3, 4, 5, and 6. Messrs Bemrose, Marion

& Co., and the Wynne Exposure Meter Co. have lent the blocks of figures 2, 7, and 10 respectively, and the Council of the Institution of Civil Engineers that of figure 8.

Through the courtesy of Messrs Bemrose & Co., Ltd., Derby, Marion & Co., Soho Square, London, and Mr J. R. Gotz, Shaftesbury Avenue, London, several supplements are given, though it is to be noted that the processes illustrated are not the only ones handled by these firms.

To all these, the writer tenders his thanks.

CONTENTS

FERRIC AND HELIOGRAPHIC PROCESSES

CHAPTER I

The Ferro-Prussiate Process

Theory in Brief.—Paper is coated with a mixture of ferric salt and potassium ferricyanide: on exposure to light, the ferric salt is reduced to ferrous salt, which gives, with the ferricyanide, a precipitate of Turnbull's blue.

The ferro-prussiate can claim to be one of the oldest printing processes, for it was used by Herschel, in substantially its present form, in 1840. For simplicity and permanency it is second to none. The color of its image is not one which fits the process for regular and systematic use; but many subjects, particularly sea-scapes and cloud-scapes, river and lake scenery, and others, into the composition of which water enters, are admirably suited for reproduction by the blue process. The color of the blue image can be altered in various ways, though not always with the most satisfactory results.

The paper for blue printing is best sensitised at home rather than bought ready-made. The amateur

may not be able to make a paper that will keep a long time, but he will have no difficulty at all in preparing one that will give far better results than much of the paper obtained in commerce.

Here, then, is the simplest and most easily worked formula. Make two solutions:—

(1) Ferric am. citrate (red),	80 grains.	183 grams.
Water, . . .	1 ounce.	1000 c.cs.
(2) Potass ferricyanide, .	60 grains.	137 grams.
Water, . . .	1 ounce.	1000 c.cs.

Unless the ferricyanide crystals are pure ruby red, wash them for a moment or two in a little water, as directed on page 118, before weighing. When the two salts have been separately dissolved, mix the two solutions in a stone bottle (previously well cleaned), or in a bottle encased in a light-tight tin, and keep well corked. The mixed solution will keep in the dark for a long time (months), but requires filtering just before use. This is an important point, and should on no account be omitted, even if the solution has been recently mixed. The filtration need only take a minute or two, provided a suitable paper and funnel is used, and the former properly fitted (see page 100).

If a little bichromate of potash be dissolved in the sensitising solution—in the proportion of half a grain per ounce or one gram per litre—the paper will keep considerably longer than if prepared with the plain mixture; but paper is so very readily coated that this addition is not really necessary.

As explained in the chapter on paper, a very great

Ferric & Heliographic Processes

From Marine Engeneer.

variety of papers can be coated with the sensitising solution, if a good arrowroot sizing be first given. The beginner will find it best to use a thin paper like Rives, which does not absorb too much sensitiser. Pin the sheets down to a clean board, placing a piece of blotting-paper underneath, and coat the paper as evenly as possible with a fine Turkish sponge. You will find it quite easy to give a very uniform coating. Coating the paper must, of course, take place by gas-light or very weak daylight, as used for toning. The paper must be dried as quickly as possible in the dark—in a drying-oven or at a moderate distance from the fire. It should be kept as dry as possible. As to how long the sensitised paper will keep in good condition, a great deal depends on the quality of the paper and on the sizing. Good paper, lightly sized, keeps longest, whilst a low-grade paper, with heavy sizing, speedily deteriorates.

On exposure to light behind a negative, the color of the paper gradually changes through bluish-green and bluish-grey to olive-green. A fully exposed print has a choked-up appearance in the shadows, whilst, with some papers, excessive over-exposure produces a peculiar bleached appearance of the shadows. On removal from the frame, the print can be kept for a day or two, though it is better to develop within a few hours.

Development consists in merely washing the print in water till the soluble salts are removed. The process may be assisted by gently rubbing with a soft sponge. Many waters contain carbonate of lime in solution, which gradually decomposes Prussian blue,

so that as short a washing as possible, commensurate with removing the soluble salts, is to be aimed at. Half an hour to an hour in frequent changes is ample, but with some waters it is not possible to give this without distinctly weakening the prints. In these cases a little citric acid should be added to the wash waters to counteract their alkalinity; then a final washing in two or three changes of plain water. A paper which prints very much more quickly, and is just as satisfactory in other ways, is made by coating with a mixture containing green ferric ammonium citrate instead of the red. This salt, the use of which is due to Valenta, can be had from Dr Theodor Schuchardt, Chemische Fabrik, Goerlitz. Two solutions are made as before:—

Ferric am. citrate (green),	110 grains.	250 grams.
Water, ...	1 ounce.	1000 c.cs.
Potass ferricyanide, . .	40 grains.	90 grams.
Water, ...	1 ounce.	1000 c.cs.

Equal volumes, mixed together, make the sensitising solution, which keeps just as well as that made with red citrate.

A still more rapid paper is prepared in an entirely different way. Uranic salts, when exposed to light, are reduced to uranous salts, and if the exposure takes place in the presence of a ferric salt, the uranous salt reduces the ferric salt to the ferrous state, becoming itself thereby oxidised back to uranic salt, and ready to be affected by light again. This action, coupled with the direct action of light on ferric salts, confers upon paper, coated with a mixture of the two

salts, a high degree of sensitiveness. Papers, prepared in accordance with these facts, were described by Alleyne Reynolds before the Sheffield Photographic Society in 1889, but appear to have attracted little attention. Reynolds' formula for coating was a mixture of equal volumes of a saturated solution of uranic chloride and a 40 per cent. solution of ferric sodic oxalate. A simpler formula, which the writer finds to answer very well, is:—

Green ferric am. citrate,	110 grains.	250 grams.
Uranic nitrate,	35 ,,	80 ,,
Water,	1 ounce.	1000 c.cs.

This is applied to paper in the usual way, and prints in the frame to a rather faint image, which is developed on a solution of potassium ferricyanide:—

Potass ferricyanide,	22 grains.	50 grams.
Water,	1 ounce.	1000 c.cs.

The blue image at once makes its appearance, and the print has only to be washed in water in the usual way.

A large number of formulæ for the ferro-prussiate process have been published, and while for simplicity and certainty the writer can recommend the foregoing, one or two others may be added.

Chambon* gives:—

Gum arabic,	88 grains.	200 grams.
Ferric am. citrate,	131 ,,	300 ,,
Tartaric acid,	88 ,,	200 ,,
Distilled water,	2 ounces.	2000 c.cs.

* *The British Journal of Photography*, 16th Dec. 1898.

Dissolve completely, and add:—

Liq. ammonia,	192 mins.	400 c.cs.

Shake well, and add:—

Potass ferricyanide,	110 grains.	250 grams.
Distilled water,	1 ounce.	1000 c.cs.

Mix thoroughly, and allow to stand a quarter of an hour before use. The color of the prints is improved by—

Eau-de-javelle,	25 mins.	50 c.cs.
Water,	1 ounce.	1000 ,,

followed by thorough washing.

Lagrange* gives:—

Ferric am. oxalate,	44 grains.	100 grams.
Oxalic acid,	4 ,,	10 ,,
Distilled water,	1 ounce.	1000 c.cs.
Potass ferricyanide,	44 grains.	100 grams.
Water,	1 ounce.	1000 c.cs.

Use equal parts.

Other formulæ, specially for engineering work, will be found in Chapter X.

* *Phot. Wochenblatt*, 1887, p. 418.

CHAPTER II

Toning Blue Prints

Blue prints can be toned to several other colors, and a large number of formulæ have been published at one time or another. Many of these do not come within the sphere of practical photography, for they merely enable a tone to be obtained which is very frequently only a sorry apology for one which can be obtained much more readily by some other process. For instance, the kallitype and Obernetter processes give dark rich tones very easily, and it is a mistaken policy to torture the blue ferroprussiate image with chemical reagents, with the object of imitating these other processes.

The most satisfactory processes for altering the color of blue prints will now be given, premising the remark that, for success, the prints must be well washed, and have been made on well-sized paper, to avoid a sunken image.

Greenish-Black (*Roy's Process*).—Make a solution of—

Borax, . . .	30 grains.	70 grams.
Water, . . .	1 ounce.	1000 c.cs.

Add drop by drop sulphuric acid till the solution reddens litmus-paper. Then add 10 per cent. ammonia solution until the red color of the litmus-paper just commences to change: if too much ammonia is added, add one or two drops more sulphuric acid and try again. The liquid should just show a faint alkaline reaction. Now add:—

Powdered catechu, .	4 grains.	10 grams.

and shake well. Nearly all the catechu dissolves. The solution is filtered and is ready for use. The washed print is placed in the above solution and removed at the stage desired. Catechu occurs in commerce in several varieties,* and the tone varies with them, ranging from greenish-blue to greenish-black. Keep the solution as cold as possible: there is then least liability for the high lights to become stained, a defect of most of the toning processes, though less noticeable with catechu than with the others. Wash the prints for a few minutes after toning.

The permanency of prints toned by Roy's process—which the writer considers the most satisfactory of all—may perhaps be regarded by some as somewhat doubtful. Catechu, however, is one of the most permanent dyes, and the tone obtained may be very fairly compared with those of platinum prints toned by Packham's process. The latter, as the experience of many during the past few years has proved, may be regarded as permanent.

* *The Photogram*, 1896 (Dec.), p. 299.

Brown Tone (*Tannin Process*). — Place the dry prints in—

Liq. ammonia (·880),	6 mins.	125 c.cs.
Water, . . .	1 ounce.	1000 „

As soon as the color has disappeared, rinse for a few minutes and transfer them to—

Tannic acid, . .	9 grains.	20 grams.
Water, . . .	1 ounce.	1000 c.cs.

In this solution the prints will gradually assume a brown color. The intensity of the brown deposit is increased by adding a drop or two of the ammonia bath to the tannin solution, but the procedure is apt to cause stained high lights.

Purple-Brown (*Bolle's Tannin and Pyro Process*).— Make a hot solution of tannic acid and add a trace of pyrogallic acid :—

Tannic acid, .	22–35 grains.	50–80 grams.
Pyrogallic acid, .	Trace.	Trace.
Water, . . .	1 ounce.	1000 c.cs.

Immerse the print in this for a minute or two until the blue gives way to lilac. Rinse, and place for a moment or two in a caustic potash solution.

Caustic potash, .	4–9 grains.	10–20 grams.
Water, . . .	1 ounce.	1000 c.cs.

The process should be conducted as quickly as possible, but a rose-colored tinge in the high lights is unavoidable, which, for some subjects, may be an improvement.

Violet-Black (*Gallic Acid and Pyro*).—Bolle recommends the following process, with which, however,

the writer has not been successful in obtaining anything but weak and sickly-looking prints. Place in—

Carbonate of soda (cryst.),	22 grains.	50 grams.
Water, ...	1 ounce.	1000 c.cs.

In this the print changes to pale yellow. Rinse slightly, and place in—

Gallic acid, . .	4 grains.	8 grams.
Pyrogallic acid, .	¼ „	·6 „
Water, . .	1 ounce.	1000 c.cs.

With gallic acid alone, violet tones are produced, whilst, by increasing the proportion of pyro, a blacker image results.

Lilac (Bolle's Process).—A lilac color is produced by immersing the print in a hot solution of acetate of lead (sp. gr., 1·24). The prints are then well washed. These lilac prints can be toned still further by placing them in a 35 per cent. solution of potassium sulphocyanide, pressing between blotting-paper, and drying before a fire: or a better plan is to add a few drops of lead acetate solution to the sulphocyanide, completing the process as just mentioned. The mixed bath of lead and sulphocyanide must be made fresh for each batch of prints.

The color has the obvious disadvantage of not resisting moisture, in the form of perspiration from the hands, damp air, etc. The image, too, fades appreciably in a strong light, and regains its original intensity in the dark. Its most useful application seems to be in toning blue transparencies for lantern slides.

Black Tones (*Lagrange's Process*).—Well wash the prints, give a final rinse in *distilled* water, and, in a yellow light, bleach in—

Silver nitrate,	9 grains.	20 grams.
Distilled water,	1 ounce.	1000 c.cs.

Well wash, first in distilled water, fume with ammonia, expose to light, and develop with ferrous oxalate developer.

Modified Blue.—

Sulphuric acid,	4 mins.	8 c.cs.
Water,	1 ounce.	1000 ,,

gives a greenish tint to the blue.

Washing with some kinds of tap water reduces the intensity of the blue and at the same time modifies its color. Some hours' immersion gives an exceedingly agreeable blue, particularly for large prints, for which, very often, the ordinary blue is too bright.

According to H. H. Buckwalter,* the following process gives a very pleasing blue. Place the print in water for a few seconds, then into—

Liq. ammonia (·880),	1 min.	2 c.cs.
Water,	1 ounce.	1000 ,,

in which it bleaches and turns a peculiar purple. When sufficiently reduced, place direct into—

Monsell's salt,	27 grains.	62 grams.
Water,	1 ounce.	1000 c.cs.

for about two minutes. Monsell's salt is basic ferric sulphate. Wash for five minutes on removal from the iron bath.

* *Canadian Photographic Journal.*

Brightening the Color.—The blue color is improved by several baths, applied after washing out the ferricyanide. One is—

Alum, . . .	11 grains.	25 grams.
Water, . . .	1 ounce.	1000 c.cs.

Another—

Oxalic acid, . .	14 grains.	30 grams.
Water, . . .	1 ounce.	1000 c.cs.

Immerse for about thirty seconds and wash again in water. A weak solution of citric, nitric, and other acids, potassium bisulphate, bleaching powder, are among other reagents which answer the same purpose.

Intensification to a slight extent is possible by immersion of the prints in a solution of an iron salt, which intensifies probably by combining with ferricyanide occluded by the blue deposit. Immerse in—

Ferric chloride, .	2 grains.	5 grams.
Water, . . .	1 ounce.	1000 c.cs.

Reduction is a process which is similarly limited in its application. Long washing is the most successful reducer of slightly overprinted proofs. A chemical reducer is:—Immerse in a weak solution of caustic potash till the lines become clear and the ground grey. Then transfer to weak hydrochloric acid till the blue color comes back: then well wash.

Titles, etc., can be written with the oxalate solution given on page 96.

CHAPTER III

The Uses of Blue Prints

The simplicity of the ferro-prussiate process will at once suggest many uses for it.

Trial Prints.—In the first place, it is eminently suited for making trial prints from negatives. In this country, photographers mostly sample their negatives on gelatino-chloride paper: in America, the blue print is in continual use for test purposes. When making the print, a piece of paper, about half an inch longer than the negative, should be used, this additional portion being shielded from light during printing by a piece of opaque paper. The print is thus obtained with a white strip along one edge, on which can be written particulars of the exposure, subject, etc., of the negative.

Negative Register.—These prints bound together in lots of twenty-five or fifty make a most useful negative register. The prints are numbered to coincide with the negatives themselves, and it will be found a great convenience to be able to turn up a positive copy of the negative, bearing particulars of exposure, character of negative, etc., instead of looking up the negative itself.

Printing on Tour.—To the tourist in foreign countries, who is anxious to make prints of those negatives which he develops *en route*, the process is to be commended. He may take a supply of paper sealed up, but better a small ruby bottle of sensitising solution and a small sponge. A few minutes' work, after the development of the negatives at night, will place him in possession of the necessary paper on which to print from them the following morning.

Illustrated Post-Cards.—The same sensitising solution can be called into requisition for producing the illustrated post-card, which seems to have found permanent favour in the eyes of the travelling public. A sensitising solution which has been specially recommended for this purpose is as follows:—

Ferric am. oxalate, .	30 grains.	70 grams.
Ferric am. citrate, .	30 „	70 „
Water, . . .	1 ounce.	1000 c.cs.

Sensitise with this solution and develop on—

Potass ferricyanide,	44 grains.	100 grams.
Water, . . .	1 ounce.	1000 c.cs.

Transparencies on glass as well as on paper are within the scope of the process; the latter, particularly, are useful for decorative purposes. For lantern slides and other glass transparencies, glass is cleaned thoroughly and coated with a gelatine mixture:—

Nelson's No. 1 gelatine,	22 grains.	50 grams.
Water, ...	1 ounce.	1000 c.cs.

Rinse the gelatine once or twice with water, stand it aside for an hour or so, then dissolve in the water (by warming the two on a water-bath), and filter hot through cotton. Warm the solution to about 130° Fah., and pour over the plates. Place them on a cold horizontal slab to cool, and, as soon as set, dry, preferably in a drying oven.

Instead of coating plates with gelatine, ordinary lantern plates can be fixed without exposure to light, and well washed or spoiled lantern plates can sometimes be used for the purpose, after removing the silver image. Farmer's reducer is frequently recommended for this, but is very liable to leave a yellow stain. A better reagent is :—

Sat. sol. of potass cyanide in water, . .	15 mins.	12 c.cs.
Sat. sol. of iodine in alcohol, . .	5 „	4 „
Water, . . .	3 ounces.	1000 „

after which the plate is well washed.

The plates are immersed for about five minutes in the sensitising solution (page 8), the surface rinsed from sensitiser, and dried in the dark. Printing takes place in the usual manner, except that, unless a special opal transparency frame is used, the process cannot be watched. It is not difficult, however, to form an idea of its progress by looking through the back. Print far deeper than for a paper print, and wash in water as usual.

Collodion has been recommended as a vehicle for

the sensitive iron salts.* G. Ardaseer gives the following formula :—

Pyroxyline (high temp.),	120 grains.	7·8 grams.
Methylated alcohol (·820),	6 ounces.	170 c.cs.
,, ether, . .	5 ,,	140 ,,

Make this a day or two before using. Allow to settle, and pour off the clear collodion. Edge the plates with indiarubber solution (in benzole), flow the collodion over, and as soon as set immerse in the sensitising liquid.

Opals, matt or glazed, can be produced by the same methods given above for glass positives, and, given suitable subjects, make very charming ornaments for the shelf or bracket.

Transparencies on Paper.—Print very much deeper than for an ordinary print, and, after washing and drying, render translucent by one or other of the well-known methods. One of the simplest is to iron small pieces of paraffin wax into the print with a smooth iron, hot enough to melt the wax. Pieces of best paraffin candle will answer, and the process can be carried out more quickly than by ironing by immersing the print in the melted wax. To do this, get your workroom warm and place the wax to melt in a basin standing in almost boiling water. Warm a zinc tray before the fire, make the print quite dry, and place in the tray. Quickly pour the wax into the tray, and before it sets remove the print. If too much wax is taken up, the print must be warmed before the fire, drained, and pressed between blotting-

* *Photography*, 1891, p. 863 (Dec. 31).

paper. Castor-oil, as described on page 96, may also be used, but always leaves a very slight greasy feeling.

The trouble of waxing can be avoided by sensitising translucent paper (as used by draughtsmen for tracing) as recommended by Hinsdale Smith,* who uses a brand of paper known as 'French parchment.' These tracing papers can be obtained in sheets, 20×30, 30×40, or 40×60 inches, from large engineering stationers like Gill & Sons, Charterhouse Street, E.C., and can be sensitised like ordinary papers by pinning to a board. The transparencies when finished can be mounted on glass or between two thin cut-out mounts.

Imitation Tiles.—The similarity of the color of ferro-prussiate prints to that of the old Delft pictures makes them a fitting medium for preparing imitation tiles, as suggested by Oscar Bolle. Select suitable bold and vigorous subjects, and after the prints are completed, mount on glass or well seasoned wood. Next, size twice with glue (one part) dissolved in water (10 parts) and varnish with good 'oak' or 'church' varnish.

Decorative.—Many little knick-knacks can be ornamented with blue prints made on paper, card, or other material. Bookmarks made from slips of Whatman's rough drawing-paper look very effective when they bear a neatly vignetted landscape, printed in Turnbull's blue.

For newspaper illustration work (where the print is to be drawn over for reproduction) a lightly printed blue print answers as well as the bleaching process,

* *Anthony's International Annual*, 1889–90, p. 218.

used with plain or matt-gelatine paper. The drawing is made with Indian ink and the faint blue image escapes reproduction when the negative is made. The oxalate of potash solution given on page 96 might, of course, be used for bleaching a too deeply impressed print.

For educational work in schools and colleges the blue process finds a place. Many lecturers distribute small prints of complicated diagrams, etc., to the members of their class for their future study at home, and when the light permits its use, the simplicity and cheapness of ferro-prussiate recommends it for this work. In dull weather gelatino-bromide must be used, though the uranium process (page 10) is worth a trial.

In the laboratory the blue print has been found most useful* in recording results of experiments, duplicating notes, etc.

* Chas. H. Himes, Ph.D., *Photographic Times*, 1896, p. 187.

CHAPTER IV

Ferro-Prussiate in Tri-color Work

The pure blue color given by the ferro-prussiate process has naturally been utilised in recent tri-color work by the superposition method. The tri-color print by W. E. Brewerton medalled at the Royal Photographic Society's exhibition of 1898, had its blue image in ferro-prussiate, and its yellow and red images in transparent inks by the gum-bichromate process. Mr Brewerton has kindly furnished the writer with particulars of the method employed by him, from which the following is quoted :—

"Having produced our three good negatives, we first commence to print on ferro-prussiate paper with the negative taken through the red screen. It is very difficult to procure a ferro-prussiate paper which is suitable for the gum-bichromate process. I find a paper sold by Messrs Marion & Company, in rolls, is the best for the work: it must, of course, be absolutely fresh. Care must be taken not to get the blue print too dark, as this will spoil the finished work. Thoroughly wash in several changes

of water, blot on clean white blotting-paper, and immerse in a saturated solution of potass bichromate (as used by the Autotype Company). Leave in soak three minutes, and hang up to dry in a dark room.

"While the blue print is drying, take half an ounce of 'Stock solution' (gum-arabic, 2 ounces, water, 5 ounces, prepared the day before), add half an ounce of water, and stir in the red color, which must be thoroughly ground with a glass muller. The transparent photo colors of Messrs A. B. Fleming & Company will be found most excellent for the process. Mix some of the ground color with the gum and water, and stir well. The exact proportions of color with gum solution cannot be very well given, as different results require different consistencies, but about one part of color to three parts of gum solution is a fair proportion, which practice will enable the operator to vary according to his requirements.

"Now quickly coat the sensitised surface of the blue print (which has been pinned down to a board) with the mixture, using a hog's-hair brush: the important point is, get the pigment over the whole surface of the paper very evenly and quickly. Finish off with a soft camel's or badger's hair brush. The sensitised paper is then allowed to dry, which takes about half an hour in a warm room—of course, in the dark.

"We now take the negative produced through the green screen, and carefully register the print upon it by holding the two up to the light—gas or

yellow light will do very well. It may not exactly register. If too large, slightly warm the print evenly all over. If too small, which is usually the case, pass it rapidly over the top of a jug containing hot water: this will expand the paper to its proper size.

"When the print and negative coincide exactly, place them in a printing frame and expose to a diffused light for from fifteen to thirty minutes —the precise time can only be found by practice. Having printed the picture, place it in cold water face downwards for two or three minutes, change the water several times, and commence the washing away of the soluble parts. This, I need hardly say to those who have used the gum process, is the most difficult part of the proceedings. Very great care should be taken in manipulating the print, and many methods—running water, sawdust and water, brushes, etc.—can be used to wash away the soluble gum and color. I myself find a piece of cotton wool the most suitable. A rough print on P.O.P. or ferro-prussiate paper should always be kept in sight, when washing away, as a guide to the removal of the soluble parts.

"This washing being completed, the double print is then before you (blue and red), and often presents a very pleasing appearance. It now requires the yellow image, which is printed from the negative taken through the blue screen as just described for the red, though I might mention that the yellow requires much less exposure."

Another tri-color process which may be mentioned

is that of Dr Noack,* who prints the red image first by a modification of Feer-type. The paper is then resensitised with a solution of lead ferricyanide, and a yellow image obtained, after exposure, by treating with potass bichromate solution. Lastly, the blue image is obtained by again sensitising—Valenta's formula (page 10)—followed by exposure and washing in water. There is considerable room for improvement in this process, which, in its present state, presents many practical difficulties.

CHAPTER V

The Kallitype Process

Theory in Brief.—Paper, coated with a mixture of ferric salt and silver nitrate, gives, on exposure to light, an image in ferrous oxalate, which, on a suitable solvent of ferrous oxalate being applied, precipitates an image in metallic silver.

This process, which, it will be seen, is on the same lines as Herschel's 'chrysotype,' was patented by W. W. J. Nicol † in 1889, and in the original form in which it was placed upon the market the silver salt

* *British Journal of Photography*, 1898, page 822 (Dec. 23) from *Phot. Correspondenz.*

† English patents, 5374 (1889), 4269 (1890), 7312 (1891).

was contained in the developer instead of on the paper. The incorporation of the two salts in the sensitive film, as subsequently patented, greatly simplifies the process, which is in fact one of the easiest to work, and affords opportunity for obtaining a variety of tones.

A sensitising solution which gives first-rate results is that of W. K. Burton:—

Ferric oxalate,	75 grains.	172 grams.
Silver nitrate,	30 „	69 „
Distilled water,	1 ounce.	1000 c.cs.

Weigh out the ferric oxalate and place in a stoppered bottle: add the water, place the bottle in a saucepan of water, and gradually raise the temperature, shaking the bottle till the ferric oxalate dissolves. Any ferrous oxalate contained in the ferric salt is left undissolved, and unless the liquid is quite clear the solution should be passed through a paper filter (page 100). Then add the silver nitrate, and store in the dark. Instead of weighing out the solid oxalate, which is a somewhat expensive salt, the solution of the same, made as described on page 118, can be used, when the above formula will stand thus:—

20 per cent. sol. ferric oxalate,	409 mins.	852 c.cs.
Silver nitrate,	30 grains.	69 grams.
Water to make,	1 ounce.	1000 c.cs.

A pure paper must be used. Saxe or Rives, Whatman's drawing-papers, and good cartridge-papers are all suitable. It is found that the paper has considerable influence on the tone. Cartridge-papers give warm sepias with great readiness, but do not

yield engraving blacks. Whatman's drawing-papers, on the other hand, do not give a warm brown at all easily.

Coat the paper (pinned to a board) with a tuft of cotton wool or fine sponge. The writer prefers the latter. Squeeze all surplus sensitiser from the sponge, and draw broad strokes across the paper, afterwards crossing the direction of these to get as uniform a coating as possible. Allow to lie for a minute or so for the solution to sink slightly into the paper. A too superficial coating gives an image which is liable to be rubbed off int he after-treatment. Then dry quickly in front of a clear fire at such distance that the paper does not become appreciably warm to the hands. Over heating will cause fog.

Very rough paper requires greater care in sensitising, to ensure the solution reaching the depressions in the paper. Work in plenty of gas or lamp light, and apply the solution thoroughly by dabbing gently with cotton wool (W. K. Burton).

Paper will keep some days wrapped in paper, but is best preserved in calcium chloride tubes, in which it will keep for months.

Printing takes place rather more rapidly than P.O.P. The image makes its appearance in the same manner as in the platinotype process, though exposure is complete when a rather less vigorous image of the shadows is produced. Detail at this point should be faintly visible in the densest portions of the negatives in bluish-brown on the pure yellow ground. Keep the paper dry during printing by backing with oil cloth or rubber. Damp paper makes it difficult to

judge when exposure is correct. If kept dry, the paper can be stored for a reasonable time before development.

Developer for Black Tones.—

Borax, . . .	44 grains.	100 grams.
Rochelle salt, .	33 „	75 „
Water, . . .	1 ounce.	1000 c.cs.
Potass bichromate sol. (1 per cent.)	45–55 mins.	94–115 „

The bichromate solution contains:—

Potass bichromate, .	4½ grains.	10 grams.
Water to make, .	1 ounce.	1000 c.cs.

Its action is to restrain, and its quantity can be adjusted to suit different types of negatives. Too little bichromate causes muddy prints with stained high lights; too much destroys the half tone.

Immerse the print face up in this solution and remove any air bubbles with the finger or a piece of glass rod. The image attains its full depth in a few seconds, but the prints must be allowed to remain from fifteen minutes (at least) to half an hour, in order to completely dissolve all iron salts in the paper. Neglect of this is the cause of yellow stains in the finished prints. Do not overwork the developing baths or the vigour and colour of the prints will suffer. Ten ounces (300 c.cs.) will develop five to six dozen half-plates. When not in use, keep the baths in the dark.

Rough surfaced prints must not be rubbed over each other in the developing or other baths: the friction of one rough surface over another is liable to

rub off the silver image, causing a mottled appearance of the print (W. K. Burton).

Developer for Purple.—

Borax, . .	12 grains.	28 grams.
Rochelle salt,	44 ,,	100 ,,
Water, . .	1 ounce.	1000 c.cs.
Potass bichromate, 1 per cent. sol.	45–55 mins.	94–115 ,,

Developer for Sepia.—

Rochelle salt, . .	22 grains.	50 grams.
Water, . . .	1 ounce.	1000 c.cs.
Potass bichromate, 1 per cent. sol.	25–30 mins.	52–62 ,,

Developer for Maroon Tones.—The following has been recommended:—

Rochelle salt, . .	44 grains.	100 grams.
Soda tungstate,	22 ,,	50 ,,
Water, . . .	1 ounce.	1000 c.cs.

Fixing Solution.—

Liq. ammonia (·880),	6 mins.	12 c.cs.
Water, . . .	1 ounce.	1000 ,,

The prints are transferred direct from the developer into this bath, and are turned over frequently for ten minutes; they are then given a similar treatment in a second bath for the same time. Fixing being thus completed, they are washed in running water for about a quarter of an hour and dried.

Engraving black tones are obtained by developing with sodium acetate, followed by a solution of potassium oxalate, to render the iron soluble.

Developer.—

Sodium acetate, . .	66 grains.	150 grams.
Water, . . .	1 ounce.	1000 c.cs.

Oxalate Bath.—

Potass oxalate,	80 grains.	183 grams.
Water, . .	1 ounce.	1000 c.cs.

Wash for a few minutes in several changes, and fix in ammonia solution as before.

Kallitype prints can be fixed in thiosulphate of soda solution instead of ammonia, though not without suffering a slight alteration in tone. W. J. Brooke * considers that greater permanency is hereby secured, and gives the following formula:—

Sod. thiosulphate, .	44 grains.	100 grams.
Ammonia (·880), .	12 mins.	25 c.cs.
Water, . . .	1 ounce.	1000 „

PRINT-OUT KALLITYPE is included in Nicol's patent specification: potassium oxalate is added to the sensitising, the formula for which is given as follows:—

Ferric oxalate, .	66 grains.	150 grams.
Potass oxalate, .	13 „	30 „
Silver nitrate, .	13 „	30 „
Distilled water, .	1 ounce.	1000 c.cs.

If slightly damp, the paper prints fully out in the frame and is fixed in—

Soda citrate, . .	13 grains.	30 grams.
Citric acid, . .	2 „	5 „
Water, . . .	1 ounce.	1000 c.cs.

* *Photography*, 1898, p. 823 (Dec. 15).

Brooke * gives the following formula for print-out kallitype :—

Ferric oxalate,	75 grains.	172 grams.
Potass oxalate,	10 ,,	23 ,,
Silver nitrate,	30 ,,	69 ,,
Water (distilled),	1 ounce.	1000 c.cs.

The exposure required is about three times that for developed paper. Fixing in sodic citrate and citric acid (see above) is all the after-treatment required beyond the usual final washing.

After-treatment of Kallitypes.—The prints can be bleached in—

Hydrochloric acid (sp. gr., 1·2),	8 mins.	17 c.cs.
Water,	1 ounce.	1000 ,,

well washed, exposed to light, and developed with metol or other developer. Strong developer gives black tones; a weak one, warm tones (red-brown, etc.), which can be further changed to purple in a sulphocyanide toning bath, single or combined.

For toning with platinum use the following bath :—

Potass chloroplatinite,	$\frac{3}{4}$ grain.	1·7 grams.
Citric acid,	$\frac{1}{4}$,,	·6 ,,
Water,	1 ounce.	1000 c.cs.

Uranium toning can also be applied successfully to kallitype prints, if due care be taken to thoroughly remove all soluble iron salts.

Kallitype for Newspaper Work.—Kallitype prints

* *Photography*, 1895, p. 778 (Dec. 5).

have been used for preparing drawings for process reproduction. A print is taken in sunlight or by the electric arc, developed, fixed, washed, pasted on a sheet of glass, and dried. The lines are put in with waterproof Indian ink and the print bleached with bichloride of mercury. When finished with, the print is removed from the glass by soaking in water.

Permanency of Kallitype.—The fact that the chemical *rationalé* of kallitype printing favours the conclusion that the image is metallic silver has been assumed by some writers as sufficient guarantee of its permanency. It should, however, be borne in mind that when in a finely-divided condition silver, like platinum, is apt to carry down certain compounds of iron, to which very often the color of the deposited metal is due. The criticisms passed on Carey Lea's work on the so-called allotropic forms of silver will call to mind this characteristic property of the finely-divided metal. In the case of platinum prints, no reaction between the iron and the platinum need be feared, but silver is a metal more susceptible to chemical change, and it is possible that it may undergo gradual oxidation by traces of associated ferric salt. There is no doubt that numbers of kallitype prints have stood the test of time for six years or more, whilst others have faded.

Hence the task of obtaining permanent prints resolves itself into the complete removal of iron salts from the paper, and attention is therefore best directed to the proper sizing of the paper, with a view to prevent the iron salt attaching itself to the fibre of the paper, and to a thorough treatment with

alkaline and neutral solvents of iron salts. Toning with gold or platinum may, of course, be done, but the simplicity and cheapness of kallitype is at once discounted and one might as well use platinotype right away.

CHAPTER VI

The Obernetter Process

Theory in Brief.—Paper is coated with a mixture of ferric and cupric chlorides. The former of these is reduced on exposure to light to ferrous chloride. In the presence of moisture the ferrous chloride reduces the copper salt to cuprous chloride (Cu_2Cl_2). On immersion in potassium sulphocyanide solution, cuprous sulphocyanide (white) takes the place of the cuprous chloride. After washing out the excess of salts, the white image is developed with potassium ferricyanide or other reagents.

This process, which takes its name from its inventor, J. B. Obernetter, was published in 1864, and gives quite easily a variety of tones which there is very good reason to regard as permanent.

Obernetter's original formula for coating the paper is:—

Copper chloride, . . .	100 parts.
Ferric chloride sol. (sp. gr. 1·5),	13 ,,
Hydrochloric acid, . . .	12 ,,
Water, ...	1000 ,,

The writer prefers to increase the proportion of ferric chloride in the above formula. A paper is thereby obtained which gives a more visible image and yields prints of greater vigour.

A suitable proportion is 30 grams of anhydrous ferric chloride (46 c.cs. of B.P.* sol., sp. gr. 1·42). The modified formula is as follows:—

Ferric chloride (B.P. sol., sp. gr. 1·42),	22 mins.	46 c.cs.
Copper chloride, .	44 grains.	100 grams.
Hydrochloric acid, .	5 mins.	10 c.cs.
Water, . . .	1 ounce.	1000 ,,

A strong paper, such as Steinbach ferro-prussiate, should be used and should be well sized. A solution of gum-arabic (10 grains per ounce or 23 grams per litre) brushed over, answers well. The paper is floated for two minutes on the above solution and dried in artificial light. The paper, which is not so sensitive as albumen paper, keeps very well indeed before exposure. It is printed until a very faint image appears, it being rather more difficult to judge the right point than in platinotype printing. Development must follow exposure as soon as possible,

* B.P. = *British Pharmacopœia.*

within two hours at the latest. If longer than this elapses, the cuprous chloride gradually reverts to the state of higher oxidation and after twenty-four hours the paper can be exposed afresh.

The developer contains:—

Potass sulphocyanide,	5 grains.	12 grams.
Sulphuric acid (conc.),	¼ min.	·5 c.cs.
Sensitising solution,	5–6 mins.	10–12 ,,
Water, . . .	1 ounce.	1000 ,,

This forms a deep red solution which deposits a small precipitate after standing some time. This may be neglected and the clear solution decanted for use. The developer can be used over and over again.

Float the paper for three or four minutes, face down, then gently immerse: float the next, agitating the liquid as little as possible during these operations. The prints may be immersed for from five minutes to half an hour. When all have been treated, transfer to a dish of clean water and wash in running water for an hour. A very faint image is visible on removal from the sulphocyanide bath, but this almost entirely disappears on washing. At this stage of the process the prints may be dried and put away until convenient to make the image visible by the action of the next bath.

Potass ferricyanide, .	44 grains.	100 grams.
Water, . . .	1 ounce.	1000 c.cs.

This solution gives a red or terra-cotta coloured print. It acts only slowly, but the prints require no attention. An immersion of several hours does no harm, and is, in fact, generally necessary. When the desired tone

and intensity is reached, wash in running water for a quarter of an hour or so, and dry.

The red prints, thus produced by ferricyanide, can be further toned through a series of tints by immersion in an acid-iron solution. To insure the success of the toning process, the prints must be thoroughly washed free from ferricyanide, or blue stains result. The toning solution is:—

Ferric chloride (cryst.), .	57 grains.	130 grams.
Ferrous sulphate, . .	145 „	330 „
Hydrochloric acid, .	123 „	280 „
Water, ...	1 ounce.	1000 c.cs.

In this bath the red tone gradually passes through reddish-violet, blue-violet, and black to greenish-black. The prints are then washed in one or two changes of water, acidulated with hydrochloric acid, then in plain water, and dried. It need hardly be said that the greatest care must be exercised in keeping the last quoted solution and the ferricyanide separate. Traces of one carried into the other on fingers or prints will produce blue stains wholesale. The strongly acid character of the toning bath necessitates a stout paper and careful handling.

A purple-violet tone resembling a silver print is produced by washing the prints for a minute or two from the iron solution and placing them for a few seconds in a very weak solution of acetate of lead.

Other tones can be obtained (after washing out the ruddy developer of sulphocyanide of iron) by silver nitrate and by permanganate of potash. The former is used in weak (2 per cent.) solution and gives a

cold black image, the print being afterwards fixed in water containing a little oxalate of ammonium. The exposure, for development with silver nitrate, must be much shorter; the exact point is rather difficult to hit.

Potassium permanganate is dissolved in water and a few drops of ammonia added. The strength of the mixture is not very important, and the bath gives brown tones. The writer's experience is that the ferricyanide and iron toning baths are preferable to either of the two last named.

CHAPTER VII

The Uranotype Process

Theory in Brief.—Uranic salts exposed to light yield uranous salt, which gives, with potassic ferricyanide, a red image of uranous ferricyanide.

The use of uranium salts for printing dates back to the very early days of photography, but uranium processes have never come into extended use. A uranium paper was made (until recently) by the Photo Company, Limited, Gray's Inn Road, London, under a patent which gives a quicker printing paper than that prepared according to the usual formulæ.

The ordinary uranium process is, however, very simple, and for obtaining certain colored images is superior to any other. The sensitising solution is:—

Uranium nitrate,	88 grains.	200 grams.
Water to make, .	1 ounce.	1000 c.cs.

Paper is floated on this solution for about five minutes, and dried before the fire as quickly as possible. The pale lemon-colored paper must be kept quite dry by storage in a calcium tube.

Uranotype requires a vigorous, even hard, negative. It is useless to expect good results from a thin, flat negative, and printing should be carried out in sunlight to get the best results. The uranium image—purplish-brown — is much more visible than that obtained with kallitype or platinotype, and it is quite easy to judge when exposure is complete. The exposed paper, however, possesses the peculiarity of gradually losing its image when kept in the dark, so that it is obvious that development must follow exposure fairly soon, and that over-exposure can be readily corrected.

Preliminary Washing.—Before development with ferricyanide, the paper is washed for ten minutes or so in several changes of water. Those, who have used uranium for toning bromide prints, will know that the use of a current of water for washing is liable to give rise to patchy prints, and that, therefore, moving the prints in a dish of still water is preferable to more energetic treatment in a print washer. This washing being completed, the print is ready for development.

Developer.—

Potass ferricyanide,	55 grains.	125 grams.
Water, . . .	1 ounce.	1000 c.cs.

The prints can be immersed in this developer, or it can be applied with a camel-hair mop or tuft of cotton wool. The print develops in a few seconds to a clear Bartolozzi red.

Final Washing.—Ten minutes' washing in several changes of water completes the process, so far as the red print is concerned.

Toning the Red Print.—The red uranium image is amenable to considerable treatment with iron and cobalt salts, and yields, according to the precise process adopted, prints in sepia, green, or blue.

Sepia and Green.—

Cobalt nitrate, .	30 grains.	69 grams.
Ferrous sulphate, .	90 „	206 „
Water, . . .	1 ounce.	1000 c.cs.

In this solution the washed, red print rapidly passes from red, through sepia, to green. To obtain intermediate colors, it is necessary to remove the print at once and to plunge it into a large dish of water. Then it is washed for a minute or two, changing once or twice, pressed between blotting-paper, and dried before the fire.

Another bath recommended by the Photo Company, Limited, for green tones is :—

Cobalt nitrate, .	1½ grains.	3 grams.
Ferrous sulphate, .	3 „	7 „
Citric acid, . .	12 „	28 „
Water, . . .	1 ounce.	1000 c.cs.

in which the prints are allowed to remain all night.

Blue Prints.—Immerse in—

Ferrous sulphate, .	100 grains.	230 grams.
Nitric acid, . .	8 minims.	17 c.cs.
Water, . . .	10 ounces.	1000 c.cs.

Fixing.—Prints which have been toned in either of the three foregoing baths must be afterwards passed into a fixing bath of—

Citric acid, . .	44 grains.	100 grams.
Water, . . .	1 ounce.	1000 c.cs.

where they remain for ten minutes. Twenty minutes' washing in several changes completes the process.

Purple Tones.—Instead of developing with ferricyanide, chloride of gold can be used to produce an image of metallic gold. The prints must be deeply printed, washed as usual, and developed in—

Gold chloride, .	4 grains.	·25 grams.
Water, . . .	1 ounce.	30 c.cs.

This is followed by several minutes' washing.

Local development, with ferricyanide solution, can be carried out just as in platinotype by thickening the solution with glycerine.

CHAPTER VIII

Prints on Fabrics—Prints in Dyes

Silk, Nainsook muslin, fine linen and cotton fabrics can each be used as a support for the sensitive coating, and, besides offering facilities for pictorial effect in large sizes, make it possible to turn out decorative articles of domestic use such as d'oyleys, mats, antimacassars.

The fabrics should be as pure as possible. Many low grades of silk are so weighted with mineral matter as to make them quite unsuitable. Purchase a fine quality silk and wash thoroughly in hot water; allow to very nearly dry and iron flat.

The fabric must be well sized to keep the image on the surface. Arrowroot is one of the best. Immerse the fabric in a thin gelatinous solution of arrowroot for a few minutes, pin down to a board, and dry before the fire. The fabric should be slightly stiff after drying. An arrowroot and gelatine size is recommended by E. A. Robins.*

Arrowroot, . . .	50 grains.	10 grams.
Nelson's gelatine, . .	18 „	3–5 „
Alum, ...	11 „	2 „
Water, . . .	12 ounces.	1000 c cs.

* *The Photogram*, 1897 (June), p. 171.

The sensitising solution (ferro-prussiate, kallitype, etc.) is brushed over, and the fabric dried as quickly as possible. For effective prints the negative should be broad in subject, of vigorous density, and without a superabundance of detail. Often negatives which have been discarded as too hard for paper printing will be found to possess the characteristics requisite for decorative work on fabrics. If they are to be made specially, photo-mechanical or lantern plates should be used and development adjusted to get contrasty negatives.

Ferro-prussiate prints on fabrics will not withstand washing in soap and water, as the free alkali destroys the blue image. A process for replacing the blue image by various adjective dyes has been developed by Stewart E. Carter.*

Bleached cotton or linen fabric is brushed over with a ferro-prussiate sensitiser made as follows:—

Ferric am. citrate, .	164 grains.	375 grams.
Water, . . .	1 ounce.	1000 c.cs.
Potass ferricyanide,	164 grains.	375 grams.
Water, . . .	1 ounce.	1000 c.cs.

Use equal parts. Expose and wash as usual. The blue print is next immersed in a weak solution of caustic soda.

Caustic soda sol. (sp. gr. 1·35), . .	12 mins.	2–5 c.cs.
Water, . . .	10 ounces.	1000 „

* *Journ. Soc. Chem. Indus.*, 1898 (May), p. 436, and *British Journal of Photography*, July 7, 1898.

The strength of this solution is approximately—

Caustic soda, . .	5 grains.	1·1 grams.
Water, . . .	10 ounces.	1000 c.cs.

It is next well washed in hot water and placed in—

Sodium hyd. phosphate,	13 grains.	3 grams.
Water, . . .	10 ounces.	1000 c.cs.

for three minutes at a temperature of 170° Fah. This is followed by washing first in cold and then in hot (160° Fah.) water, after which the print is ready to receive the dye.

A weak gelatine solution is made:—

Glue size, . . .	24 mins.	5 c.cs.
Water, . . .	10 ounces.	1000 c.cs.

This is heated to 160° Fah. and the prints moved about in it for two or three minutes, from three to five grams per litre (1·3 to 2·2 grains per ounce) of dinitro-resorcine (resorcine green) is added, and the temperature raised to 180° Fah. As soon as the shade is considered full enough for a strong picture, remove to boiling water, to wash out all unfixed dye. The whites are next cleared in a bath of neutral soap (used at 160° Fah.) and the print again washed in hot water and finally in cold. Other dyes besides resorcine green can be used. Gallocyanine gives violet and blue; alizarin gives purple; alizarin brown, sepia.

CHAPTER IX

Heliographic Processes Compared

Heliographic copies of tracings have become such an indispensable aid to the engineer, architect, and others that there is no need to recommend them here. A few words may, however, be said on the comparative utility of the several processes.

It should be noticed that the terms positive and negative, as applied to these processes, are held to have meanings as follows:—A 'positive' paper is one which gives, from an ordinary line tracing, a copy in dark lines on a white ground: a 'negative' paper is one which gives, under similar circumstances, a copy in white lines on a dark ground.

For large work the chief processes are four in number:—

Process.	*Copy from line tracing.*
Ferro-prussiate.	White lines on blue ground.
Pellet.	Blue ,, ,, white ,,
Ferro-gallic.	Black ,, ,, ,, ,,
Brown.	White ,, ,, brown ,,

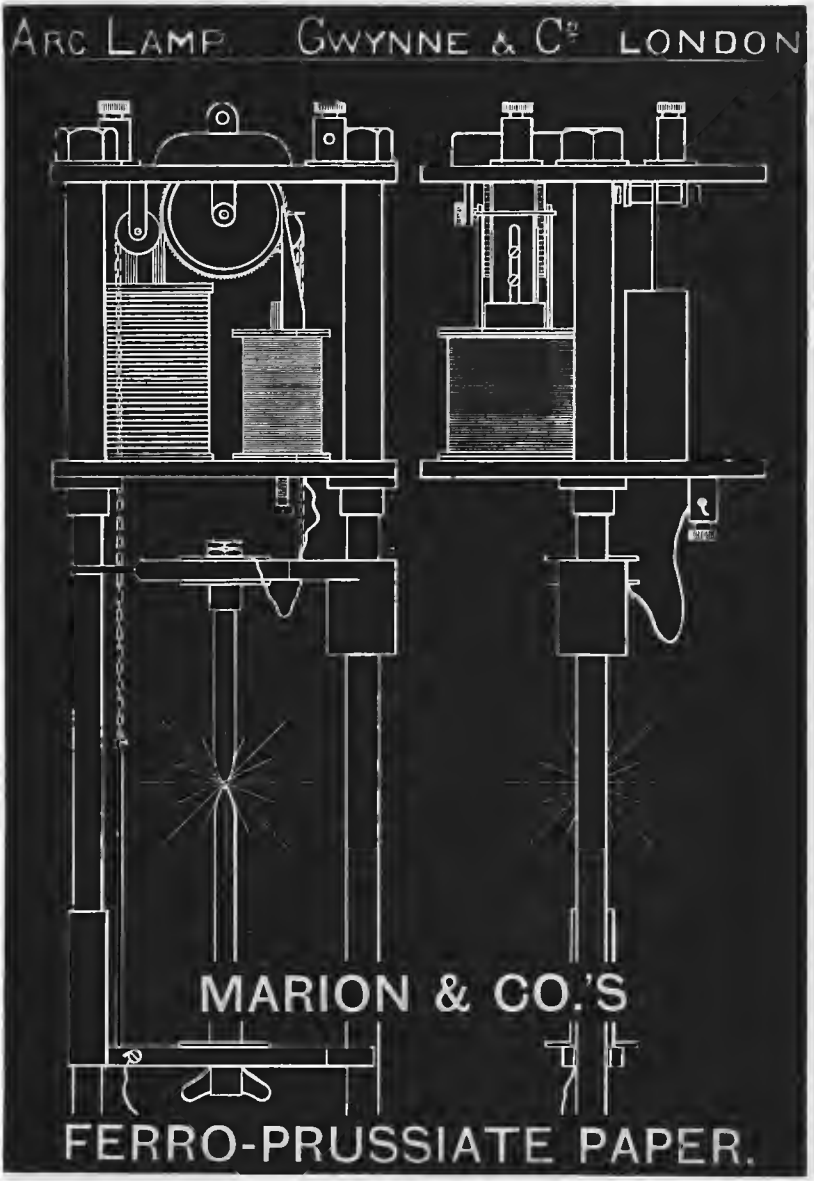
Ferro-prussiate is the simplest and cheapest of these. It requires only the slightest experience to

work it successfully, and necessitates the smallest outlay in the way of baths and space. Formerly its slowness in printing was one of its chief disadvantages, but paper is now obtainable which almost rivals 'Pellet' paper in rapidity. Its blue ground is the chief objection which draughtsmen urge against it, though the writer has often heard mechanics and others (who use blue prints in the shops) say that they prefer them to the white ground copies.

'*Pellet*' *paper* is known by various other names, such as 'Cyanofer,' 'Positive Ferrotype,' 'Cyanographic,' etc. It is certainly the most rapid paper, and for winter work especially valuable. It requires greater skill and experience to work it, and a series (four) of baths for development and subsequent treatment.

Ferro-gallic paper is much less sensitive than 'Pellet' but scores over the latter in its simplicity of after-treatment, requiring only one chemical bath or, in the case of the 'water-developing' paper, merely washing in water. The black line is said to be preferred to the blue of the Pellet paper as giving a more truthful copy of the tracing, a preference which is purely a matter of taste and should be put alongside the fact that the ferro-gallic process rarely gives the absolutely white ground which 'Pellet' paper does, a faint violet tinge being almost always unavoidable.

The '*brown*' *or* '*sepia*' is a process which is coming into favour on account of its rapidity, simplicity, and particularly, because of its adaptability to turning


ARC LAMP. GWYNNE & Cº LONDON
MARION & CO.'S
FERRO-PRUSSIATE PAPER.

out a number of positive copies (brown line on white ground) from a negative intermediate (white line on brown ground), printed directly from the tracing (page 88).

Other processes which are used to a much smaller extent, and chiefly for fine work, are described in Chapter XVII. Platinotype (which is not there described) is also used, and gives very perfect copies. Unfortunately its expense and the precautions needed in its use preclude its general adoption, though it has been used to a fair extent for the reproduction of reduced copies of drawings. The Locomotive Department of the L. & N.-W. Railway Co. is a case in point.

Which of these processes shall be adopted by a drawing office, setting up a heliographic outfit, is a question upon which it is not easy to give advice. For occasional prints, such as an architect or surveyor is likely to require, the ferro-prussiate or ferro-gallic is best suited. For the regular routine of a factory, where a large number of prints are wanted every day and often urgently, the 'Pellet' process should certainly be installed. At any rate, the foregoing few hints will help the reader to decide for himself.

CHAPTER X

Preparation of Heliographic Papers

Ferro-prussiate—Pellet—Ferro-gallic—Brown-line

Ferro-prussiate.—Although few printing houses will wish to themselves prepare Pellet and ferro-gallic papers, the coating of ferro-prussiate paper demands so much less skill than that of these processes that many printers may very well prepare it for their own use. Apart from the question of diminished cost, the superior results, consequent on the employment of fresh paper, will make the procedure worth while.

For a satisfactory and rapid printing paper the writer recommends the formula given on page 10, which is here repeated:—

Ferric am. citrate (green),	110 grains.	250 grams.
Water, ...	1 ounce.	1000 c.cs.
Potass ferricyanide, .	40 grains.	90 grams.
Water, ...	1 ounce.	1000 c.cs.

Mix equal volumes. This keeps well in the dark, beyond requiring to be filtered just before use, and prints very rapidly.

An equally good though slower formula is:—

A. Ferric am. citrate,	1 ounce.	113 grains.	260 grams.
Water,	4¼ „	1 ounce.	1000 c.cs.
B. Potass ferricyanide,	5 ounces.	75 grains.	172 grams.
Water,	32 „	1 ounce.	1000 c.cs.

Mix equal parts (Lietze).

A standard formula is that of Fisch.*

Tartaric acid, . .	3 ozs.	153 grs.	95 grams.
Water, . . .	13 „	90 mins.	375 c.cs.
Ferric chloride sol. (sp. gr. 1·45),	2 „	390 „	80 „
Liq. ammonia (·880), not more than,	6 „	70 „	175 „
Potass ferricyanide, 2 oz. (av.) 205 gr.	2 „	360 grs.	70–80 grams.
Water, . . .	13 „		270 c.cs.

Dissolve the tartaric acid in the water, add the iron solution, and then the ammonia, with constant shaking till neutral. Add now the ferricyanide solution with constant shaking, cool, and keep in well-corked bottles in the dark.

It would be easy to multiply formulæ, but one or two from authoritative sources may be given.

C. B. Talbot† gives:—

Potass ferricyanide, .	53 grains.	122 grams.
Liq. ammonia (·880),	4 mins.	8 c.cs.
Ferric am. citrate, .	86 grains.	197 grams.
Distilled water, . .	1 ounce.	1000 c.cs.

* *La Photocopie*, p. 32, Paris, 1890.

† *The International Annual*, 1889-90, p. 233. Anthony & Co., New York.

Dissolve the ferricyanide in the water, let stand a few hours, add the ammonia and then the dry flakes of ferric am. citrate, stirring these in with a glass rod. One fluid ounce coats $1\frac{1}{2}$ square yards of paper; 100 c.cs. coat $4\frac{1}{2}$ square metres.

Another very sensitive sensitiser is :—

Ferric chloride (cryst.),	175 grains.	400 grams.
Oxalic acid, . .	44 „	100 „
Water, . . .	1 ounce.	1000 c.cs.
Potass ferricyanide,	88 grains.	200 grams.
Water, . . .	1 ounce.	1000 c.cs.

Mix the two solutions.

The rolls of paper are sensitised on a table about half an inch narrower than the width of the roll.

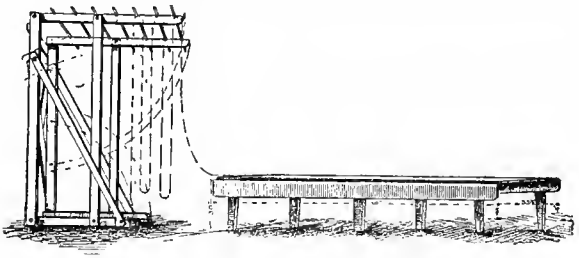


Fig. 1.—Coating and Drying Paper.

A roller at one end of the table delivers the paper as required, and a drying frame at the other end serves to receive the coated paper in serpentine folds for drying. The top of the drying frame is provided with six or eight detachable rods, which are slipped underneath the paper as each table-length comes from the coater's hands, and placed in slots provided for them in the frame (fig. 1). By enclosing the drying

frame in a closet, in the lower part of which a coil of steam or hot water pipes is fixed, the paper is quickly dried (C. B. Talbot).

Coating should be done with a fine sponge, taking off any surplus sensitiser with a second sponge, only just moist with sensitiser. The dry coated paper should be of a greenish-yellow colour, and must be kept as dry as possible in a moderately warm place. Damp is fatal to its keeping properties.

Coating paper in wholesale quantities by machinery does not come within the scope of this work, and the reader is referred to Eder's *Ausführliches Handbuch der Photographie*, Part IV., pp. 224–227, for drawings and particulars.

Pellet.—(Blue line on white ground).

This process is perhaps best known by the name of Pellet, who brought it to perfection, though Pellet's formula is a trade secret.

A formula for coating due to Pizzighelli is one which the writer can recommend.

Three stock solutions are required:—

A.	Pure gum arabic,	88 grains.	200 grams.
	Water,	1 ounce.	1000 c.cs.
B.	Ferric am. citrate,	220 grains.	500 grams.
	Water,	1 ounce.	1000 c.cs.
C.	Ferric chloride (cryst.),	220 grains.	500 grams.
	Water,	1 ounce.	1000 c.cs.

The gum solution keeps only a few days, the other two for many weeks, if kept well corked in the dark.

To make the sensitiser take :—

Sol. A. (gum), . . .	20 vols.
Sol. B. (citrate), . .	8 „
Sol. C. (chloride), .	5 „

Add B and C, little by little, shaking between each dose. C must be added after B. Reversal of the order is liable to cause coagulation of the gum. The mixture is thick at first, but becomes thinner after a few hours. It keeps in good condition for two or three days.

Fisch * gives another formula :—

Gum arabic (Senegal),	128 grains.	175 grams.
Water, . . .	1 ounce.	600 c.cs.

When completely dissolved, filter through muslin, and take the specific gravity. It should be about 1·090. If more than this, add water little by little, shaking well, and testing with the hydrometer. The solution only keeps a few days.

Tartaric acid, . .	175 grains.	40 grams.
Water, . .	1 ounce.	100 c.cs.

This ought to have a specific gravity of 1·075 : if more, add water as above.

Ferric chloride sol. (sp. gr. 1·45).

To compound the sensitiser take :—

Gum solution,	20 ounces.	1000 c.cs.

Add little by little, shaking well :—

Tartaric acid solution,	1 oz. 6½ drams.	90 c.cs.

* *La Photocopie*, p. 15.

Well mix, and add slowly, with constant shaking:—

Ferric chloride solution,	2 oz. 3 dr.–2 oz. 5 drms.	120–130 c.cs.

Test the mixture with the hydrometer. The gravity should be 1·080: add water (well mixing) until it registers this figure within a division or two.

The paper for the Pellet process must be well sized and calendered to resist the penetration of the sensitiser into the fibre. This is necessary to avoid blue staining of the ground. Special papers are sold by Steinbach, Blanchet Frères, Kleber, and other makers.

Coating is by brushing or floating. For the former, spread the sensitiser as evenly as possible with a large badger brush, working the brush first lengthways and then crosswise very lightly, to get a uniform coat. The happy medium between a too thin and too thick coating is what is wanted. The former gives prints of poor vigour, the latter requires a longer exposure to obtain a pure ground.

To coat by floating, Duchochois directs rolling the paper up, sized side outwards, and placing the roll on the solution contained in a dish. The two ends of the roll are slowly drawn out, with the result that the paper gradually unrolls itself and is drawn away coated with the sensitiser. It is dried quickly in the dark, and keeps for a long time preserved from light and damp.

Ferro-gallic.—For development with gallic acid, paper is coated with a mixture containing ferric chloride and tartaric acid with gum or gelatine.

Colas, to whom the perfection of this process is largely due, give the following formula :—*

Gelatine, .	14 grains.	33 grams.	10 grams.
Ferric chloride (syrupy),	29 „	67 „	20 „
Ferric sulphate,	14 „	33 „	10 „
Tartaric acid,	14 „	33 „	10 „
Water, .	1 ounce.	1000 c.cs.	300 c.cs.

This is applied in the same manner as the sensitising solution in the Pellet process.

Lietze in his comprehensive treatise on heliographic printing recommends† the following :—

Gum arabic, . .	1 ounce.	67 grams.
Ferric chloride (solid),	$\frac{3}{4}$ „	50 „
Tartaric acid, . .	$\frac{1}{2}$ „	33 „
Monsell's salt, . .	$\frac{1}{2}$ „	33 „
Water, . . .	15 ounces.	1000 c.cs.

For Monsell's salt see page 17. Development takes place in gallic acid solution (one part of acid in 320 parts of water).

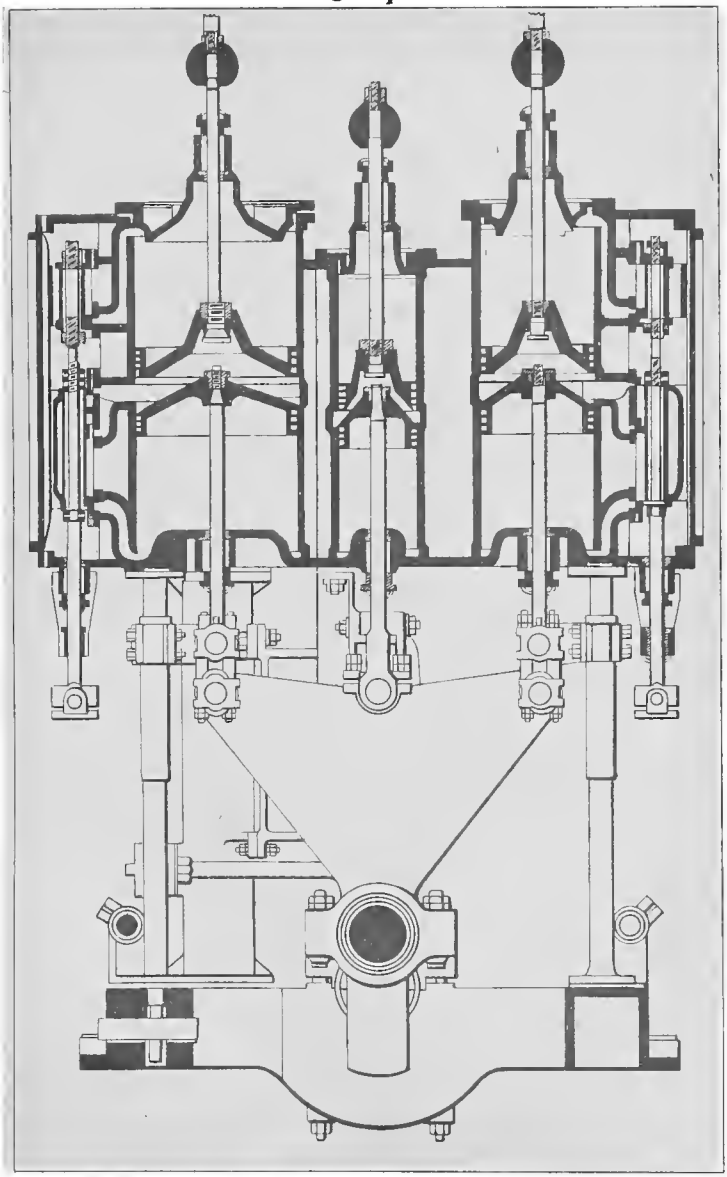
Another recent formula is Nakahara's :—‡

Gum arabic,	59 grains.	135 grams.	15 grams.
Tartaric acid, .	8 „	18 „	2 „
Sod. chloride (salt),	36 „	81 „	9 „
Ferric chloride, .	59 „	135 „	15 „
Ferric sulphate, .	39 „	90 „	10 „
Water, .	1 ounce.	1000 c.cs.	110 c.cs.

* *Gewerbeblatt aus Wurtemberg*, 1886, vol. xxxiii. p. 365 ; Eder's *Handbuch*, 1887, vol. iv. p. 236.

† *Modern Heliographic Processes, Instruction in the Art of Reproducing Drawings, Engravings, etc., by the Action of Light.*

‡ *Photo Chronik*, 1895, p. 125 ; *The Amateur Photographer*, March 29, 1895.



From „Engineering" May 5. 1899.

Dissolve the gum in the water (hot) and add the rest of the chemicals in the order given. Apply the mixture to the paper with a sponge; then, squeezing out the sponge, remove as much as possible.

Ferro-gallic—Water-bath.—By incorporating gallic acid or other developing substance with the salts on the paper in such a manner that no reaction takes place between the iron salts and the gallic acid, a sensitive paper is produced which gives a black-line copy merely by washing in water. There are two methods of manufacture. According to the older, finely-powdered gallic or tannic is strewed over the paper which has received the coating of iron salts. According to the more recent method, the coated paper is treated with a solution of gallic acid containing also a substance which prevents the reaction between ferric salts and gallic acid until (when the copy is developed) this restraining substance is largely diluted with water. Hydrochloric, oxalic, and tartaric acids act in this way, and are dissolved along with the gallic acid in a solvent which can be applied to the paper without disturbing the coating of ferric salt.

A formula for the first method is that of Shawcross and Thompson, who took out a patent in 1884 (English patent, No. 8771).

Gelatine, . .	60 grains.	1,500 grams.
Ferric sulphate, .	24 ,,	600 ,,
Salt, . .	37 ,,	940 ,,
Tartaric acid, .	7 ,,	188 ,,
Ferric chloride, .	60 ,,	1,500 ,,
Water, . . .	1 ounce.	11,000 c.cs.

Finely-powdered gallic acid is dusted over the paper,

which has received a coating of the above solution and has been dried.

Paper to be treated by the second method is given a coating of a somewhat similar solution to the above, and after drying is floated on—

Gallic acid,	66–88 grains.	150–200 grams.
Tartaric acid,	22–35 „	50–80 „
Alcohol,	1 ounce.	1000 c.cs.

Paper prepared by this process develops—so it is stated by Messrs Schering, who are the makers of the paper—very much more quickly than that manufactured by the powder process, owing to the fine state of division of the gallic acid. On immersion in water, the equilibrium existing between this substance and the tartaric or other acid is upset, and the former reacts at once with the ferric salt with which it finds itself in contact.

Brown Line.—This is a silver or iron process somewhat analogous to kallitype, but demanding a very much simpler treatment after exposure. The patentees,* Messrs Arndt and Troost, of Frankfort-on-Main, give the following particulars :—

A paper must be used which contains no chlorine; that made from pure rag is most suitable. The presence of wood pulp is very objectionable.

The sensitising solution contains :—

Ferric am. citrate,	35–44 grains.	80–100 grams.
Tartaric acid,	7–9 „	15–20 „
Gelatine,	4–7 „	10–15 „
Silver nitrate,	5–9 „	12–20 „
Distilled water,	1 ounce.	1000 c.cs.

* English patent, No. 20,358, 29th June 1895 ; *British Journal of Photography*, 1895, p. 541 (23rd Aug.).

Paper is soaked in this solution and dried; it keeps unchanged for several months.

Two decompositions probably take place when the paper is exposed to light. Some of the silver nitrate forms (in combination with the gelatine) the dark coloured 'gelatinate of silver,' whilst the second and predominant reaction is that of the reduction of the ferric to ferrous salt, the latter precipitating metallic silver from the silver nitrate.

CHAPTER XI

Making Tracings for Sun-copying

Tracings for reproduction by ferro-prussiate and allied processes should be on thin bluish tracing paper. Tracing cloth scarcely gives such good copies and does not take the draughtsman's ink so well as the paper: whichever is used, a yellowish-colored tracing is to be particularly avoided. Many manufacturers of printing papers supply specially suitable tracing cloths and papers.

Lines, dimensions, etc., should, wherever possible, be drawn in thick Indian ink, and it is always well to add a little chrome yellow or gamboge, or a little of one or other of the various preparations sold for rendering the ink more opaque to actinic rays. The test of a good tracing for sun-copying is to hold it up to a

strong light and to closely examine the opacity of the lines.

Lines in colored inks never come out so well as those in Indian ink, unless an exceptional thickness of ink be used, in which case the brilliancy of the color is impaired. Prussian blue should be avoided or, if it has to be used, thickened with an opaque pigment like Chinese white or flake white. Indigo gives better results than Prussian blue, though unfortunately, if applied fairly thick, is scarcely distinguishable from black. Vermilion is the best color for red.

Wherever possible, it is best to use Indian ink lines in different styles of punctuation in place of colored inks.

It is sometimes desired to color the sectional portions of the printed copies. This offers no difficulty in the case of prints by the Pellet and ferrogallic processes, but for ferro-prussiate prints the sectional portions of the original tracing must be covered with an opaque color like Chinese white. In the printed copy these portions will be practically white, and they can then be colored as desired.

To make a tracing which can be used as a negative for ferro-prussiate paper (giving blue lines) on a white ground, the method of M. Cheysson* is to be recommended.

Make the tracing in lithographic ink. The ink is prepared by rubbing the solid stick on the bottom of a large saucer. When enough has been thus ground

* *Manual des procédés, de reproduction d'ecritures et de dessins à employer dans le service des ponts et chaussées*, Paris, 1880.

up, a very little distilled water is added (tap water is not suitable) and the whole mixed with the finger. If not of the requisite consistency, add a little more water and grind up with the ink till a dense and liquid mixture results, which is used on the drawing pen exactly like Indian ink.

Let the tracing dry and place on a board covered with one or two thicknesses of blotting-paper. With a soft brush, coat the whole surface of the tracing with a solution of aniline brown (a strong solution of the dye made in hot water and allowed to cool). Be careful to get none on the back. As soon as dry, rub the paper over with a tuft of cotton wool or soft rag moistened with turpentine until the ink lines of the drawing are dissolved away. This leaves the design in transparent lines on a dark brown ground, and the process will yield positive prints (dark lines on white ground) when printed in ferro-prussiate or brown-line processes.

Tracings must on no account be folded or creased: all such marks will show in the copy.

CHAPTER XII

Outfit for Heliographic Printing

The apparatus necessary for the equipment of a printing house is not very expensive, and comprises printing frames, baths for development and washing, drying arrangements, benches for trimming and mounting copies, and racks for keeping tracings which have or have not been copied. These, and a small room for the storage of sensitive paper, will meet the requirements of the blue printer.

The printing frame (fig. 2) is the most important item in the outfit, and consists of a strong shallow frame with a plate-glass front, on which the tracing and sensitive paper are laid. These are backed up with a thick pad of felt, preferably covered on its under side with vulcanised rubber sheet. The back of the frame is made in several sections, pressure on each being applied by means of a series of vertical spiral, or other, springs, held in place by upright pegs fixed to the back itself. These springs exert downward pressure on the back of the frame and upward on the cross-bars, which are hinged to one side of the frame and secured by a catch to the opposite side. A properly constructed frame is a *sine quâ non*, since it is most essential that the tracing and sensitive paper shall be pressed into firm and uniform contact,

Any defect in this respect means blurred lines in the copy.

A frame of different construction (fig. 3) to those usually employed is recommended by C. B. Talbot,* whose description of it is here given. The paper and tracing are put in on top instead of at the back, as usually practised. The glass plate, 48×72 inches, is

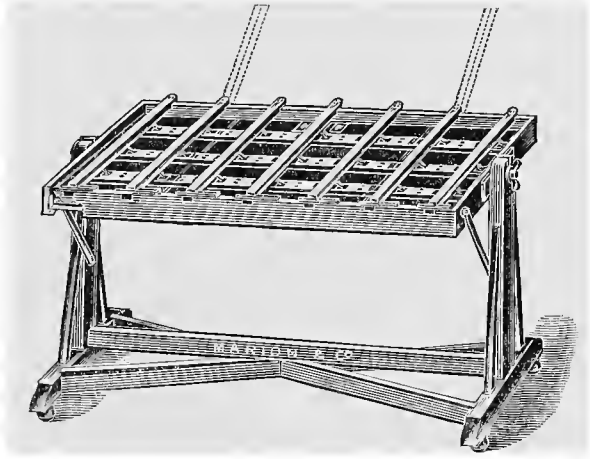


FIG. 2.—Printing Frame.

laid on the under side of the rabbet, when looking at the top, and secured on the under side to the sash by a half-inch stop, screwed to the sash of solid ash, $2\frac{1}{2} \times 4\frac{1}{2}$ inches. No putty or lead is used about it, as their use only causes fracture. The glass can move in the rabbets, when subjected to variations of heat or pressure, better than when fixed to the wood. When hooked down in place and under pressure,

* *Anthony's International Annual*, 1889–90, p. 235.

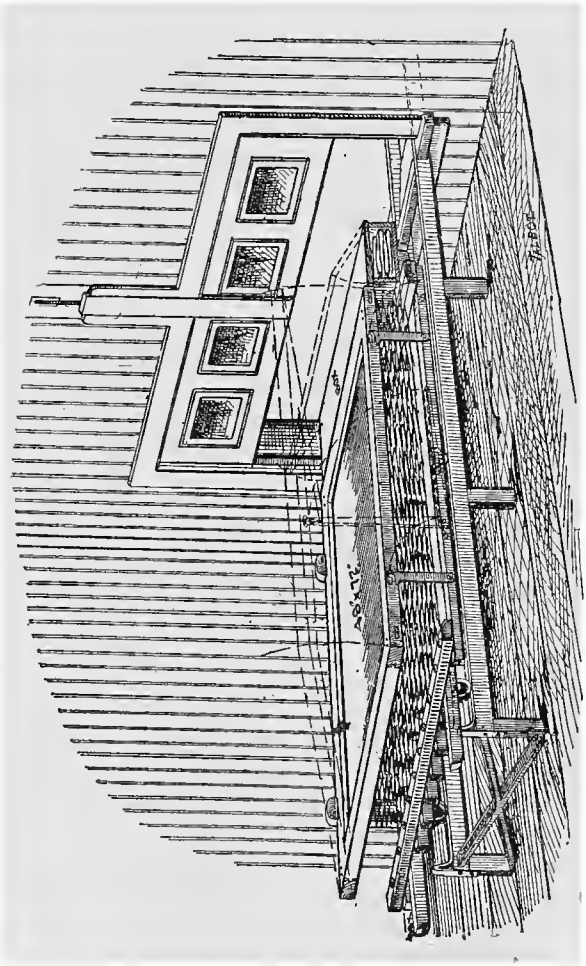


FIG. 3.—Printing Frame designed by C. B. Talbot.

the rain cannot enter any more than by the old plan of glazing. The pressure pad (fig. 4) under the glass is made of narrow boards, $5\frac{1}{2}$ inches wide and $\frac{7}{8}$ inch thick, which are cut rather more than half through in twelve places, making (as it were) thirteen blocks, in length 68 inches, being 4 inches shorter than the glass, to keep the wet on the sash in rainy weather from touching it. On the sides these boards are two inches narrower than the glass in their extreme width. Eight of these boards are laid side by side and are placed so that an ordinary cardboard will move freely in the crack between them: they are kept in place by three cross-pieces on the under side. The outside

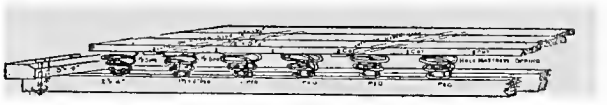


FIG. 4.—Pressure Pad. (C. B. Talbot.)

boards are screwed firm and fast to the laths, but the interior ones are left a little loose, *i.e.*, the screw heads are not quite screwed home on each board where the lath crosses it. This allows the boards to play vertically but keeps them in place laterally. Immediately under each board is a 2×4 inch joist, having thirteen pegs, $1\frac{1}{2}$ inch diameter and 2 inches long, each under the middle of each block space. On each of the pegs the small end of half a common mattress spring is placed, and the wide end of the spring secured to the under side of the boards, on the middle of each space between the cuts, by common flattened wire staples driven across the spring wire. The whole (boards and springs) is laid in place and

supported on the cross-bars below, the ends of which are bolted to 3×4 inch cross-pieces (laid across their upper edges) to hold them all together. On top, between the boards and glass, a single thickness of common felt is placed: no more than this is necessary.

In fig. 3, four wheels on $\frac{7}{8}$-inch half round iron tracks, $1\frac{1}{4}$ inches thick and 6 inches diameter, will be seen underneath the frame, set on solid axles $\frac{7}{8}$ inch diameter in brass boxes. These are for moving the printing frame into the sun. They are placed, one pair as near the back or inside end as possible and the forward or middle pair about 10 inches forward of the middle of the frame, so that the latter will nearly balance when lifted at the back end. This arrangement is for turning off the water when the frame is out in rainy weather, and for inclining it to the sun when it is rolled out of doors and exposed to light on the turntable.

The turntable is a stout hexagonal frame, through a cross-piece of which a $\frac{3}{4}$ inch bolt or pin passes into a cross-piece of the tramway on which the printing frame runs, a washer between the two slightly raising the tramway and enabling the latter, when balanced, to be easily turned in any direction.

When this has been done, the turntable is pushed a little further forward on the trucks, and now, out of balance on the washer, cannot be turned by the wind or otherwise. It is now held up by a prop (fig. 5) on a hinge on turntable and a hook over the after axle, so that no damage can come to it by wind.

In fig. 5 are seen two boxes, one at each end,

used for printing drawings longer than the glass. One edge of the tracing is pinned to the paper, the glass is raised up (as per dotted lines in fig. 3) and held so by a stick, movable on a screw in its lower end. One of the box-lids (say, the inside or rear one) is opened and a thick piece of paper *laid* over the edge of the box and on to the printing pad. The surplus paper and tracing are now folded up in serpentiue fashion in the box and another thick paper

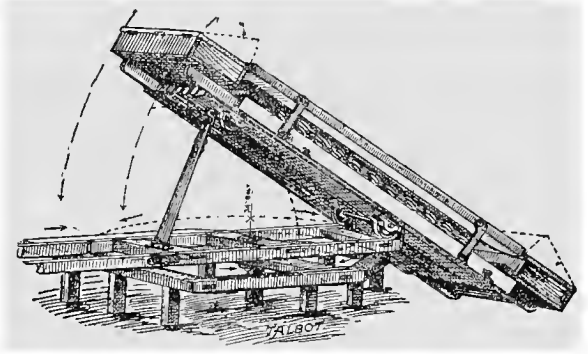


FIG. 5.—Printing Frame. (C. B. Talbot.)

laid on top between the box and sash, in order to keep the light off the paper in the interspace. Then the free end is laid on the tracing, the sensitised paper placed below, and the sash let down and examined to see that all is in place; if so, it is pushed down, locked by the hooks on the front edge of sash, and rolled out of doors. Before doing so, however, a round-edged board is laid on a marked line at the unprinted end. When printed, the frame is brought in, the printed portion folded same as before, placed

in the outside and empty box, the space between the box and the sash covered over as before, and the round-edged board placed on the glass exactly over the printed portion. On the opposite end of the glass, use a similar board as at first and continue the operation, moving the printed portion into the outside box as fast as printed. When not required for this purpose, the boxes are removed and hung up in the printing room.

A cheaper form of printing frame which does not involve the use of a glass front is also described by the

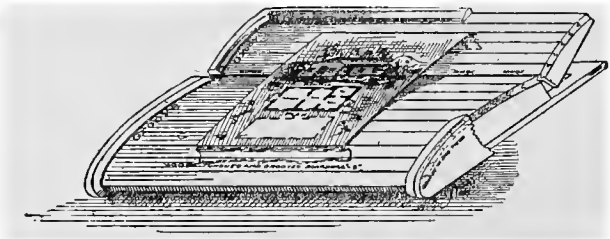


FIG. 6.—Unglazed Printing Frame.

same writer as specially suitable for field or other purposes where portability is a consideration. Two end boards (fig. 6) having an arch-shaped groove, secured to a hinged frame at the back, have placed therein the ends of some loosely-fitting tongued and grooved boards, the surface of which are formed to the radius of the curve (3 or 4 feet). Each board is about 3 inches wide and supported loosely on a bridge at the middle of the back of the same shape as the grooves. About one-third of the width of the frame is hinged. The edge of the tracing is slipped through any crack in the tongue and grooves corresponding to its width.

On the narrow side, the boards near the edge are made of different widths, say, $2\frac{1}{2}$, 3, $3\frac{1}{2}$, 4 inches, so that one edge of the tracing being placed in a given crack, the other edge is pretty certain to find a suitable hold on the other side of the hinge. The tracing with, of course, the paper beneath it is stretched by pushing the board closely, allowing the

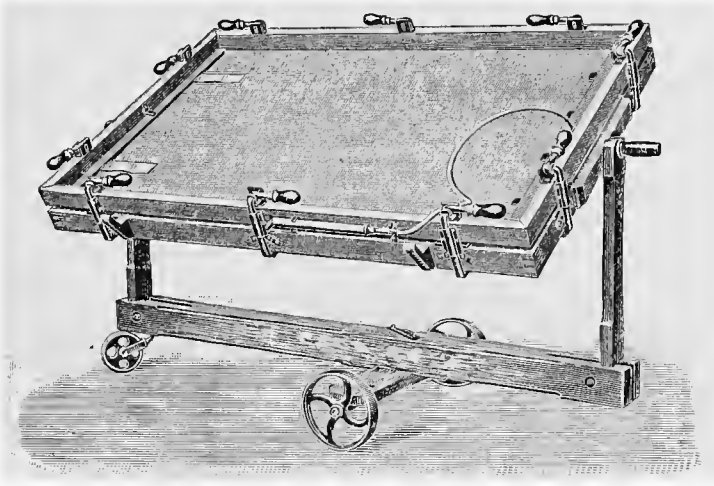


FIG. 7.—Sack's Pneumatic Frame.

tracing to slip easily though firmly through the cracks between the boards until the desired tension is given: then bringing the hinge down and locking it at the back to the frame.

A pneumatic printing frame, in which pressure is applied to the back of the sensitive paper by an inflated air-cushion, is upon the market, and is said to give very satisfactory results (fig. 7).

Very long tracings are not easily printed in the ordinary frames. The suggestion has been made by Cleaves * to print them around a circular drum having a slit in its side to allow of access to two rollers in the interior. The tracing and sensitive paper are wound together round one roller, brought out through the slit, taken round the drum, and stretched tight by means of the second roller. The drum is rotated during printing and after exposure, a second length of tracing and paper unwound from the first roller whilst the exposed portion is coiled round the second. The arrangement seems practical, but the writer has not seen it in actual use.

Washing and Developing Baths.—For washing in plain water, the most satisfactory material, taking price into consideration, is zinc, and baths of this material can be used for developing ferro-prussiate and ferro-gallic and brown-line prints, and for the final washing of copies on Pellet paper. They must not be used for the ferrocyanide and acid bath required in the Pellet process, for which lead-lined wood trays or papier-maché are necessary. Wooden wax-coated trays are readily made at a small cost and can be used for practically all the blue printers' solutions. Yellow pine is the best material, being dovetailed together, made quite hot before a fire, and melted paraffin wax poured in as evenly as possible: any irregularities can be corrected with a hot iron. The outsides of the trays should be varnished with

* Memoir by Prof. R. H. Thurston, Washington Meeting of Mechanical Engineers, 1887.

shellac varnish. Another suitable protective coating for the inside is:—

Brown resin, . .	4 parts.
Bees-wax, ...	1 part.

These are melted together and applied hot.

The baths should be of ample size: it is a mistake to stint matters in this respect. A safe rule is to have them six inches larger than the largest tracing

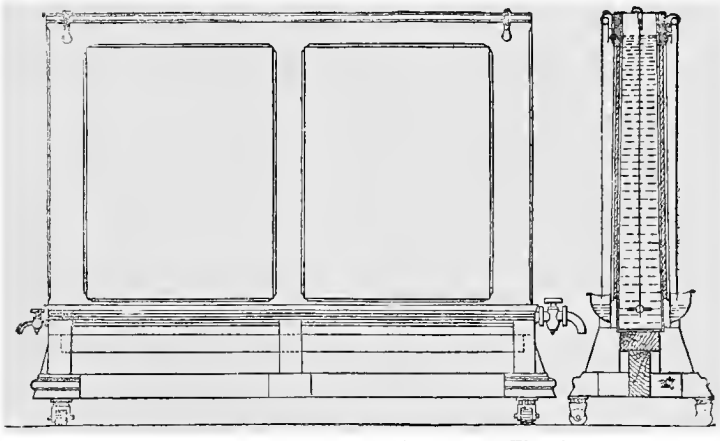


Fig. 8.—Vertical Washing Bath. (B. H. Thwaite.)

which the printing frames will accommodate. They are arranged on trestles with a water tap (with rubber tube attached) at one end. In winter an oil or gas stove or coil of steam pipes is required under the Pellet developing bath and others. Each bath should be kept for one particular purpose and no other. Neglect of this is the cause of much trouble in the matter of stains.

For office use, where space is limited, B. H. Thwaite* prefers to use a vertical washing bath for ferro-prussiate prints, suspending the copy in the water from a light lath laid across the top of the bath (fig. 8).

Drying Arrangements.—An efficient drying apparatus is described and illustrated on p. 52, and a small room—or a corner of the developing house partitioned off—fitted up with a similar arrange-

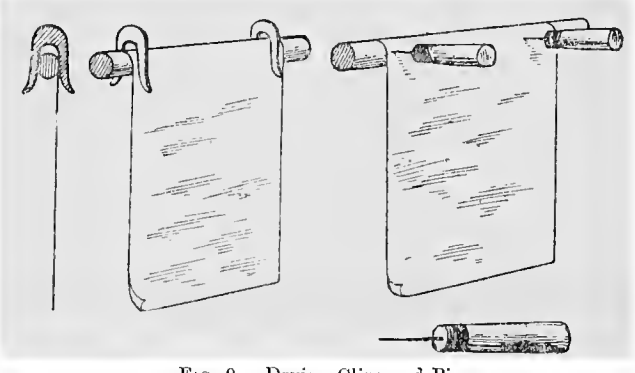


FIG. 9.—Drying Clips and Pins.

ment and furnished with a coil of steam pipes in the base and an outlet for air above, will speedily dry prints, whatever may be the state of the weather. Otherwise, a series of drying rods or lines with a gas stove fixed close at hand is a practical though less certain method. For attaching prints to the drying rods, clips, in shape of an inverted U, are used, or Kent's dark-room pins are very convenient. For attaching to lines, the usual clips are employed (fig. 9).

* *Proc. Inst. Civ. Eng.*, 1885–86, Pt. IV., p. 812.

Other Fixtures.—A couple of solid tables for trimming and mounting prints are necessary items in the outfit, as are also some racks in which to file tracings which await printing or are being retained for future use.

A small room kept warm and dry should be set apart for the storage of the sensitive papers, the opened rolls of which should be stored, when not in use, in tight tin cases.

The illumination of the place used for developing must be subdued. Weak daylight is very generally used with satisfactory results. If sunlight has to be excluded from any window, yellow tissue paper pasted on the glass will be found to answer.

The arrangement of the printing house will, of course, depend very largely on local conditions and requirements. Where space and an open view are available, a yard in front of the premises, into which the printing frames can be wheeled, is convenient. In towns it is often necessary to utilise the roof of a building for printing purposes. In offices to which daylight has no very free access, the exposure is shortened by the use of two reflectors, one outside the window, face upwards at an angle of 45° to the horizontal, and one inside, above the window and face down, at the same inclination. The light from the sky is reflected from the first mirror to the second and thence to the printing frame. Sometimes the latter can be raised to the roof and exposed to the direct light of the sky, reaching it through a fanlight.

Electric arc light can be used for printing on Pellet

paper, and several installations are in use. According to B. H. Thwaite,* the exposure required at 5 feet from a 6000 candle-power lamp is about thirty minutes, and several frames can be exposed together in a circle round the lamp.

Water Supply.—The quality of the water used for washing blue prints is a point which may in certain cases require attention. It is pointed out on p. 126 that weak alkalies—even calcium carbonate in solution—decompose *Prussian blue,* whence it follows that the 'softer' a water is the more suitable for the purposes of the blue printer. For practical purposes the quantities of carbonate of lime and other salts in most town waters have no appreciable action within the limits of ordinary manipulation. Cases do, however, arise where the water makes itself known by its weakening action on the blue ground or line of the print. An instance was recently brought to the writer's notice where a printing house was being supplied with a water containing over 40 grains of carbonate of soda (expressed as Na_2CO_3) per gallon, which speedily reduced the intensity of the prints. The application of a chemical test (the estimation of the alkalinity, etc.) will at once tell whether a water supply is unsuitable in this respect.

* *Proc. Inst. Civ. Eng.*, 1885-86, Pt. IV., p. 812.

CHAPTER XIII

Ferro-prussiate, or White Line on Blue Ground

White Line on Blue Ground.—The tracing is laid face down on the glass of the printing frame, and a piece of sensitive paper, of such size as to project about two inches all round, laid upon it. The felt pad and the back of the frame having been fixed, the whole is exposed to light, and the progress of printing judged by observing the outside portion, which gradually changes from yellowish-green through bluish-green and slaty-grey to olive-green, the tint corresponding to correct exposure differing slightly with different brands of paper. A minute or two's exposure beyond this point will (in the case of ordinary tracing paper or cloth) leave the print properly exposed. Prints from thicker and more opaque paper must, of course, receive much longer exposure, and it is generally necessary to examine the print itself.

Exposure may be gauged by meter, and for this purpose a very convenient little instrument is Wynne's print meter. The meter (fig. 10) consists of a small metal case with a front of opal and a hinged back, carrying inside a sensitive paper. Behind the opal face is a plate, perforated with a series of diaphragms, which serve to admit different intensities of light to a series of figures on a glass plate, which, when the meter is

closed, is pressed into contact with the sensitive paper on the back of the instrument. On exposing the meter to light, the light gradually impresses the graduated scale—which is numbered 1 to 16 and then onwards A to P—on the sensitive paper.

In using the meter for timing blue prints, a preliminary test exposure is made, paper and meter being

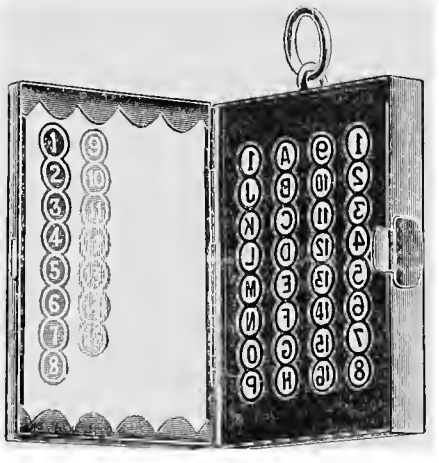


FIG. 10.—Wynne's Print Meter.

exposed simultaneously to the same light. As soon as the print is correctly exposed, the last number (just readable) registered on the meter is noted, and, in all future work with the same brand of paper and quality of tracing cloth, the print can be taken in as soon as the meter registers that particular number. Other brands of paper will require a different meter number, but, these once ascertained (by a test exposure), ex-

posures can be made with certainty. Several frames can be timed with one meter if exposed at the same time and to the same light. The meter can be used also for Pellet, ferro-gallic, and other processes.

Development.—On removal from the frame the print is washed in water. Slowly running water is best, but in its absence a soft brush or sponge is very efficient in removing the surplus salts. A thorough treatment in this way in the first water, followed by two or three short soaks in clean water, will be sufficient. Too little washing causes veiling of the lines afterwards: too much, a general weakening of the copy. Fifteen to twenty minutes is generally quite sufficient. In winter, a little more.

In cases where a print is required at the earliest possible moment, lay the copy in the bottom of the washing bath and apply a vigorous stream of water from an india-rubber tube (squeezing the end between the fingers or using a jet) to both back and front of the paper. A minute or two's treatment of this kind suffices to get rid of practically all the soluble salts.

After washing, the copy is rolled up wet and stood aside to drain: then opened out and hung up to dry in a subdued light.

Over-printed copies are given a somewhat longer washing, which, if exposure has not been greatly excessive, has the effect of clearing the lines; otherwise, it is best to throw away the prints rather than to treat them with potash or other chemical reducing agents, the results of which are generally disappointing.

Under-printed copies can be somewhat improved by

immersion in a weak solution of an iron salt, though no great intensification must be expected. Scherings make up a solution, specially for use with their blue paper, under the name of *Verstarkungslösung fur Blausäures Eisenpapier*. The well-washed print is placed in—

Stock sol, .	2·5–5 mins.	5–10 c.cs.
Water, . .	1 ounce.	1000 ,,

for about five to twenty seconds, and, as soon as the blue of the ground has deepened sufficiently, is washed in clean water and dried. The weak bath keeps several days. The usual experience is, however, that intensification is of little use, and that an under-exposed print had better be thrown away and a second copy made.

Additional lines are put in with the oxalate of potash solution (given on p. 96) thickened with a little gum-arabic.

Existing lines are removed by Prussian blue applied with a fine camel's-hair pencil.

CHAPTER XIV

Pellet, or Blue Line on White Ground

The Pellet paper is much more sensitive than most brands of ferro-prussiate, and must only be handled in quite a subdued light. The exposure in summer sunlight is about seventy seconds, but, as the image is only faintly visible, it is necessary to judge of its completion by a trial method or by meter, as described on p. 76.

Trial Method.—When the paper is being placed in the frame, a test strip of tracing cloth is placed alongside the tracing. This strip (which may measure about 6×2 inches) has ruled upon it half a dozen or more lines in Indian ink or vermilion, corresponding as nearly as may be with the lines of the tracing, and on cloth of a similar quality. A stock of these strips, in different thicknesses of ink and on different cloths, should be kept at hand, and with a little experience it is easy to select a suitable one. The strip is laid near the edge of the frame, and a few strips of sensitive paper laid crosswise behind it with the free ends projecting from the frame. When the exposure is judged to be about complete, a strip of paper is pulled out and dipped in the ferrocyanide bath for

about thirty seconds. The lines should develop to a vigorous blue, and the ground show no sign of blue stain. If the ground is blue, continue the exposure and test again. If, on the other hand, the lines are feeble and broken, exposure has been too long.

Faking during Printing.—During exposure to light a good deal can be done to make the most of inferior tracings by masking portions of the latter. Very often one part of the tracing is made in thinner ink than another, as may be seen by examination in a strong light, and the thinner parts will be saved from being feebly reproduced by masking with a soft dark cloth which can be readily fitted to the area desired. Then the outside parts of the tracing are liable to get dirty and to give a bluish ground, if exposure be timed for the lines; but if the central lined portions be covered, an additional exposure can be given to the outside, which will ensure a pure white ground in the copy.

Development.—The print is developed on a strong solution of potassium ferrocyanide (yellow prussiate of potash).

Yellow prussiate,	1 ounce.	1 pound.	100 grams.
Water, . .	10 ounces.	1 gallon.	1000 c.cs.

Use warm water for dissolving the salt and see that the temperature of the bath does not fall below about 60° Fahr. Some makers advise rather stronger, others weaker solutions than the above. Their printed instructions will supply the specific strength. The developing tray should contain this solution to a depth of from $\frac{3}{4}$ of an inch to 1 inch.

Before removal from the tray, turn up the edges of the print all the way round about half an inch, so that it forms a shallow tray. In this shape it is removed and floated on the developer, the raised edge preventing the access of developer to the back. As soon as laid on the liquid, the whole back is smoothed down with the palm of the hand so as to bring every portion into contact with the liquid (fig. 11). Then it is raised by the two nearest corners, and held up

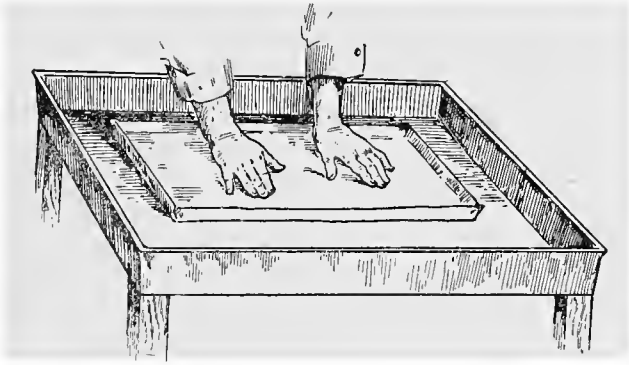


FIG. 11.—Developing Pellet Papers.

for examination. All the lines ought to be visible in vigorous blue. The time from the moment of flotation to the removal from the developer should not exceed about thirty seconds. Too long on the developer produces spreading of the lines.

Washing.—Next pass the print into a bath of water, and flush it quickly back and front from the india-rubber tube. This is merely to stop the action and remove most of the ferrocyanide, and only occupies a few seconds.

Acid Bath.—The print next passes into an acid bath (sometimes referred to as the 'fixing' and sometimes as the 'bleaching' bath). This is made as follows:—

Sulphuric acid (sp. gr. 1·98), .	1½ ounce.	40 c.cs.
Water, . . .	40 ounces.	1000 ,,

Add the acid to the water, and not *vice versa*. Much heat is produced on mixing, so that a glass vessel must not be used. Instead of sulphuric acid, hydrochloric acid can be used:—

Hydrochloric acid, .	4 ounces.	100 c.cs.
Water, . . .	40 ,,	1000 ,,

These are average strengths, but the makers' directions will give those which they consider best for their papers. Keep the print in this bath, face up, for not more than five or six minutes, occasionally stirring the liquid with a wooden spoon or with a rag tied to a stick. This bath soon turns a deep blue, but retains its solvent properties (for the insolubilised gum) for a long time.

Final Washing.—On its removal from the acid bath the print is covered with a deposit of light blue color, derived from the oxidation of the white precipitate produced by ferrocyanide on ferrous salts. This deposit is only loosely adherent, and is washed away by subjecting the print to a stiff jet of water. A soft brush can be used in default of a strong enough water pressure, but requires gentle handling to avoid weakening the lines. Be particular to keep this

washing bath clean by regularly scrubbing it with potash solution and a hard brush. Wash the print in running water or several changes for a quarter of an hour, and dry.

Defects, their Causes and Remedies.

Blue Stains in Patches.— 1. Incomplete contact of the print with the developing solution.

2. Developer getting on the back of print.

3. From stained fingers, while being finally washed.

Remedies.—Remove the blue stains with the oxalate solution given on p. 96.

Be careful to clean the fingers in weak potash solution after dabbling in the acid bath.

Uniform Blue Ground.—Under-exposure.

Faint and Broken Lines.—Over-exposure.

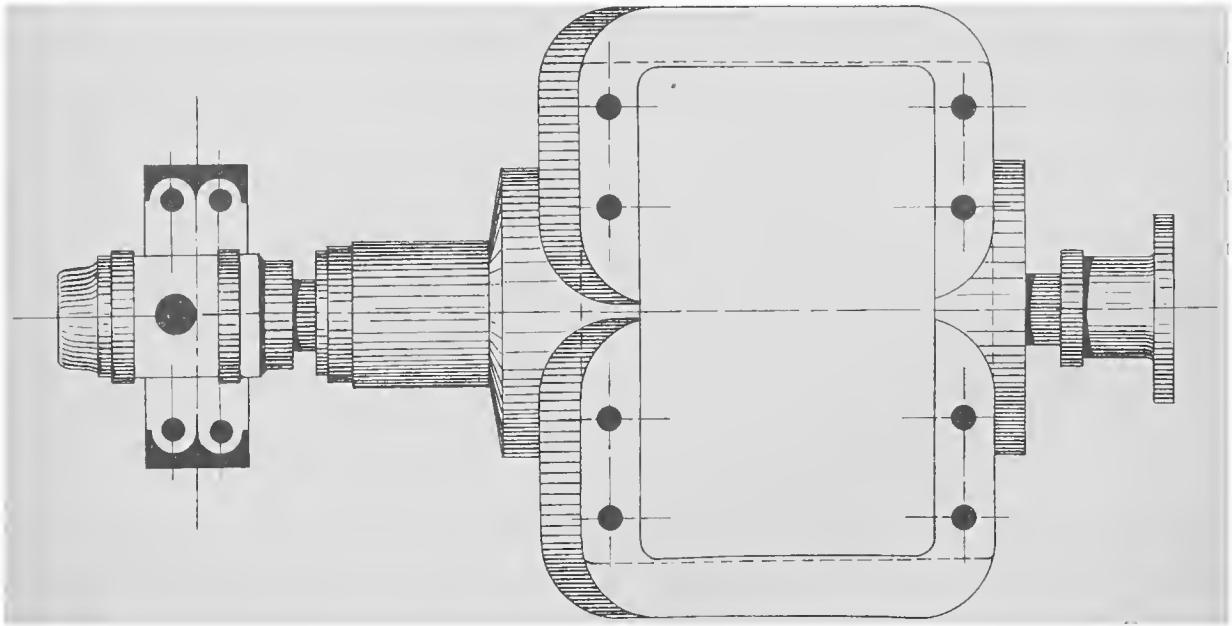
Spread and Blurred Lines.—Under-exposure. Too long development. Too strong developer.

CHAPTER XV

Ferro-gallic, or Black Line on White Ground

Gallic-Bath Process — *Exposure.* — The paper is very much slower (about five times) than Pellet paper, and requires, in summer sunlight, an exposure of about five minutes. The exposure is judged by (1) noticing when the portions of paper projecting outside the tracing become white. A corner of the sensitive paper is folded over, so that the white back of the paper provides a standard for comparison. (2) Test strip as described on p. 79, the strip being immersed in the gallic-acid bath. (3) Meter (p. 76). The writer prefers (2) and (3) to (1), which, with tracings of yellowish color, is liable to give under-exposed proofs. Whichever method is used, the correctly exposed copy is seen as yellow lines on a white ground. The sooner it is developed the better, but it should certainly not be kept overnight.

Development.—Gallic acid is the developer generally used, in conjunction with some substance to help keep the ground clear. Alum and oxalic acid (in small proportion) are used for this.



A formula which may be given is:—

Gallic acid, . .	2 ounces.	12 grams.
Alum, . . .	2 „	12 „
Water, . . .	1 gallon.	1000 c.cs.

Mix in warm water twenty-four hours before use. Immerse the print in the liquid for about three minutes. The copy develops at once to intense black lines on the ground, which is never quite white, but always has a pale violet tint. Wash in running water for a few minutes, drain, and dry.

Defects and Causes.—Violet ground with thick and blurred lines—under-exposure. Faint and broken lines—over-exposure.

Water-Bath Process.—Exposure takes place just as for the gallic-bath paper and development must follow on the same day.

Development.—Wash in running water for ten minutes or so. Under- and over-exposure cause the same defects as with gallic-bath paper.

Violet spots, lines, and unnecessary dimensions are removed by a weak solution of oxalic acid.

The directions given for the use of the ferro-gallic paper, made by Messrs Messerli of Zurich, contain a number of useful hints from which the following are quoted.

The pressure pad, whether of felt or cloth, is liable to become damp, and, when placed directly on the back of the paper, not only spoils the ground of the paper, but renders a much longer exposure necessary. This explains the considerable difference in sensitiveness sometimes noticed between pieces of paper from

one and the same roll. The moist condition of the frame is responsible for these irregularities, and not, as the printer may be inclined to think, a want of uniformity in the paper.

The fact, too, is frequently overlooked that the much weaker action of winter sunlight on the paper is in part due to the absence of heat rays, and that, if the pressure pad of the frame is thoroughly warmed, exposure takes place appreciably quicker. Before ten in the morning and after one o'clock, winter sunlight is very weak.

It is a mistake to be over-economical with the developer, which should be renewed as soon as the printer notices that the developing salt is becoming exhausted. An over-worked bath will not give an intense black tone.

A cause of failure with the ferro-gallic process is in floating the copy on the developer or in developing by drawing through the solution. Total immersion is necessary. In the after washing, the copy must on no account be allowed to remain long in water containing developer. The best way to wash is to hold the copy for five minutes under a rose jet, so that the water continually passes off.

Insufficiently exposed prints can be corrected by applying a 2 per cent. solution of tartaric acid with a sponge, and as soon as the dark ground has given way, by well washing with water. This treatment will frequently be found of service, and the solution should find a place in every printing house.

When testing a fresh batch of paper, the fact should be borne in mind that the first yard or so of the roll

seldom gives such good prints as the remainder, and the inferiority of the first portion is the more noticeable the longer the paper has been kept. A freshly made developing bath should be used, and if the paper from the first or second yard's length does not give good results, about half the paper should be unrolled and the piece exposed from the middle portion. If this likewise gives poor results, the paper may be assumed to be at fault.

CHAPTER XVI

Brown Line on White Ground

This is a paper which gives from an ordinary tracing a copy in white lines on a deep brown ground, prints very rapidly, and requires very simple treatment after exposure. The brown color of the deposit makes the process a very suitable one for preparing several paper negatives from a single tracing, each of which can be put in hand to give copies in blue line on a white ground (on ferro-prussiate paper), or brown lines on a white ground if the 'brown' paper itself be used. For getting a number of prints from a tracing, which is wanted at once for some other purpose, the process is, therefore, most useful.

White Line on Brown Ground.—The tracing and paper are placed in the frame just as for a ferro-

prussiate print and exposed to light. The time of exposure in summer sunlight is from thirty seconds to six minutes. The appearance of the print when fully exposed is a clear brown: it gains vigour somewhat in washing and fixing.

Washing.—Wash the print for about five minutes in running water.

Fixing.—The fixing bath contains:—

Soda thiosulphate (hypo.),	7 grains.	15 grams.
Water, ...	1 ounce.	1000 c.cs.

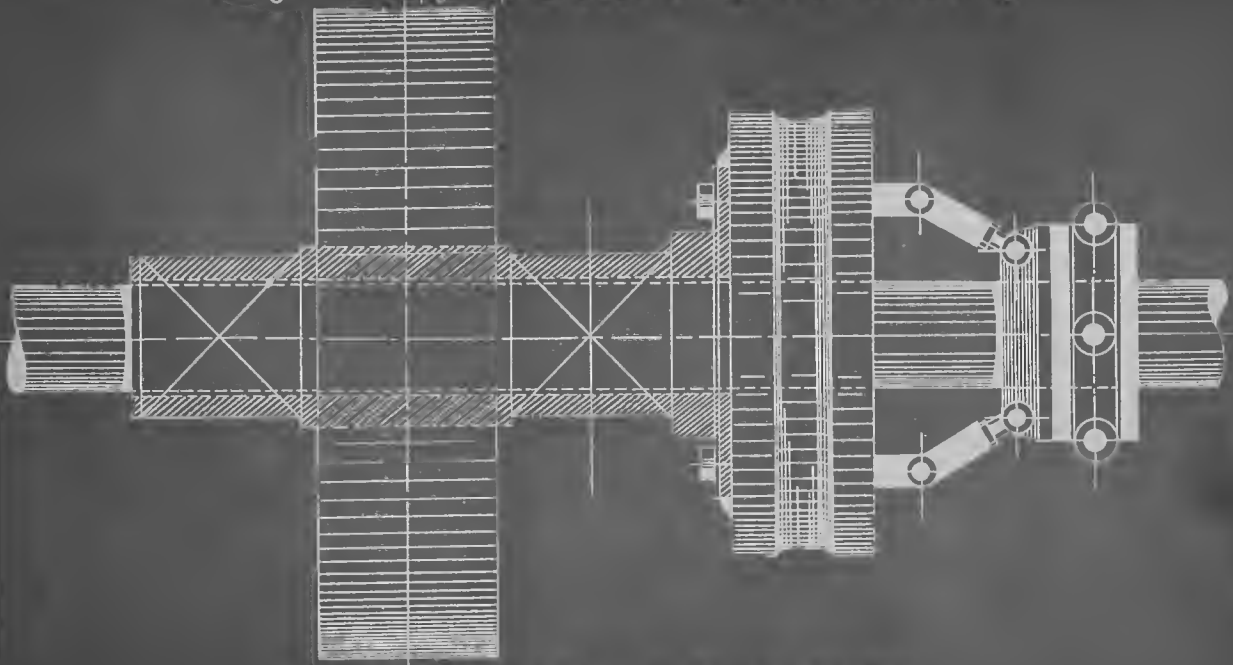
and in this the print is immersed for about a minute. The fixing solution can be applied, if more convenient, with a sponge or brush.

Final Washing.—Well wash for about fifteen minutes, and dry.

Brown Line on White Ground.—The 'brown ground' copies obtained as just described can be used for printing positive copies. A thin paper is best for this purpose, for the sake of rapidity of printing, but a thicker paper can be rendered translucent by means of castor-oil, as described on page 96. The brown-ground copy is treated exactly like a tracing, and exposure and fixation of the copy proceeded with as above described.

To remove brown lines from the 'white ground' prints, or to insert white lines in the 'brown ground' prints, use a solution as follows:—

Sat. sol. of potass cyanide in water,	15 mins.	40 c.cs.
Sat. sol. of iodine in alcohol, .	5 „	12 „
Water, . . .	1 ounce.	1000 „



CHAPTER XVII

Minor Heliographic Processes

A NUMBER of processes of minor importance are described in this chapter. Considerations of cost or of skill demanded for working them have prevented most of them from coming into general use.

With Silver Salts.—Papers (plain or albuminised) sensitised with silver nitrate, chloride, or other salts, have been used for heliographic copying, giving a copy in white lines on a dark ground from an ordinary tracing. Those who wish to employ a silver process will find it better to use the commercial sensitised paper rather than to prepare one for themselves. The only use, however, to which present-day copyists are likely to put the process is in preparing the negative from a small tracing, from which to print positive copies on ferro-prussiate or albuminised paper.

Directions for working the process will be found in any of the larger treatises on photography.*

Liesegang † describes a rapid silver paper—containing silver chloride and iodide and developed with gallic acid—which is capable of being utilised in everyday work to some advantage.

* Abney's *Instruction in Photography*; Eder's *Handbuch der Photographie.*

† *Die modernen Lichtpausverfahren*, p. 31.

Willis's aniline process gives dark lines on a white ground from an ordinary tracing, and depends on the fact that aniline reacts with chromic acid to form a blue-black coloring matter. It has been used in engineering works to a slight extent.

Paper is coated with a chromate mixture and, after exposure, is developed in aniline vapour. Sensitise a hard paper (Steinbach) by floating for one minute on—

Potass bichromate, ...	1 part.
Phosphoric acid (sp. gr. 1·24) . .	10 parts.
Water, ...	10 „

Dry quickly, and expose on same or next day. In summer sunlight the exposure required under a tracing is about three minutes. The copy appears in yellow lines on a greenish ground.

To develop, the print is placed on the bottom of a shallow box, to the lid of which are pinned several sheets of blotting-paper, soaked in a mixture of aniline oil and benzene :—

Aniline, about	1 part
Benzene, ...	15 parts.

More aniline accelerates development. The solution is spread evenly on the blotting-paper and the print left in the box to gradually develop. The correctly exposed copy commences to appear after a few minutes and gradually gains strength. The final tint of the copy is influenced by the time of development. Long exposure to the aniline gives brownish-black, whilst the shorter the development the bluer

the color. The prints are washed in water for a few minutes. During this treatment they occasionally turn green: add a few drops of ammonia to the wash water. In the industrial use of the process development is accelerated by employing a steam bath to volatilise the aniline.

Poitevin's process utilises the fact that gelatine mixed with a ferric salt is insoluble in water, but becomes soluble when the mixture is exposed to light.

The following working details are due to Abney :— Prepare a 6 per cent. solution of gelatine and add sufficient of a suitable pigment. Float paper on the warm mixture and sensitise by immersion in—

Ferric chloride,	44 grains.	100 grams.
Tartaric acid,	13 „	30 „
Water,	1 ounce.	1000 c.cs.

Dry in the dark, expose with the aid of an actinometer, and develop in hot water. The process gives a copy in dark lines on a white ground from a tracing, and while it furnishes most excellent reproductions requires great care in manipulation.

Chromate Pigment Processes.—The insolubility, etc., conferred upon gum or gelatine, when exposed to light with potassium bichromate, is the basis of several processes of this kind. They give copies in white lines on a dark ground. The following may be taken as typical of the procedure adopted.

Prepare—

Gum-arabic,	35 grains.	80 grams.
Lampblack,	9 „	20 „
Water,	1 ounce.	1000 c.cs.

Spread this mixture with a broad brush on the paper, dry, and sensitise immediately before use with—

Potass bichromate,	55 grains.	125 grams.
Water,	1 ounce.	1000 c.cs.

This solution is liberally applied to the back of the paper, which is allowed to stand for a few minutes, and the coating then equalised with a brush, just moistened with sensitising solution. Coating can be done in daylight, but the paper must be dried in the dark. The pigmented side of the paper is laid in contact with the tracing, and exposed to light till the lines of the drawing are visible on the back. This requires from ten to twenty minutes in summer sunlight. The exposed copy is dipped for a minute in pure water and laid, pigment side up, on a glass plate. The surface is rinsed with a jet of water, removed from the water, and the soluble parts of the image gently dislodged with a soft brush. This leaves the copy in yellow lines on a black ground. It is next soaked in water for several hours to dissolve chromium salts, washed in clean water, and dried. To obtain positive copies (dark lines on white ground) a negative tracing must be prepared (page 60).

Gelatine is used in place of gum in a similar way.

Positive prints are obtained by a variation of the method. The details given are due to L. von Itterheim :—

Gum-arabic,	110 grains.	250 grams.
Potass bichromate,	31 ,,	70 ,,
Alcohol,	5 mins.	10 c.cs.
Water,	1 ounce.	1000 ,,

Smooth sized paper is coated with this mixture, which keeps a few days. It is exposed under a tracing for five or ten minutes and washed in water till the lines of the drawing look engraved. It is then dried, and given an even and thin coat of shellac and lampblack.

Shellac,	1 part.
Lampblack,	3 parts.
Alcohol,	20 „

Apply this with a sponge and, when dry, immerse the paper in—

Sulphuric acid,	2–3 parts.
Water,	100 „

until the superfluous black can be removed by gentle rubbing.

Anthrakotype was devised by Sobacchi in 1879: we are indebted to Pizzighelli for precise working details. The process gives a positive from an ordinary tracing, and lines of any desired color can be obtained by selecting a suitable pigment.

Hard gelatine is mixed with cold water in the proportion of one part of gelatine to 30 parts of water, allowed to swell for an hour, and dissolved by placing the containing vessel on a water bath. It is filtered and kept at a temperature of 40–50° C. (113–122° Fahr.).

Well-sized, hard-surfaced paper is cut into sheets, which are immersed one after another in a dish of water. A thick glass plate is meanwhile levelled, and a well-wetted sheet laid thereon: a piece of sheet rubber is laid over it, and the two squeezed

together. The rubber is removed, and the edges of the paper are turned up all round about half an inch. The warm gelatine solution is poured into the tray thus formed, and by tilting the glass plate and with the help of the finger or a brush, spread over the whole surface. This done, the plate is set aside in a horizontal position and a second paper coated, the first being dried as soon as the gelatine has set. The gelatinised papers are sensitised in—

Potass bichromate, .	18 grains.	40 grams.
Water, . . .	1 ounce.	1000 c.cs.

in which they are immersed for one or two minutes, any air bubbles being detached during that time with a camel's-hair brush. Sensitise in ordinary daylight, but dry in the dark: the paper keeps good for a week.

Exposure occupies about 20–25 seconds in bright sunlight, the design appearing as light yellow on a brown ground. Over-exposure can be corrected, but not under-exposure. The printed proofs are washed in several changes of cold water, as long as the soluble bichromate colors the solution yellow. Each proof is then separately dipped in a bath containing water at 28–30° Cent. for one, or, at most, two minutes: this has the effect of slightly softening the lines of the drawing which the cold bath had brought into relief. The print is removed, laid face up on a level surface, and superfluous moisture blotted off. Fine pigment is now dusted over the paper from a fine gauze sieve and spread over the lines with a soft brush. It adheres to the lines, and should leave the ground white,

but it usually happens that, owing to ample exposure, the ground is a little colored. Subsequent washing removes this. The pigmented copy is next dried in a warm place (in summer, in the sun; in winter, near a fire or in a drying oven) at a temperature not above 60° C. (140° Fahr.). It is then soaked in cold water till limp, the ground cleared from superfluous color with a soft wet sponge, and, finally, again dried. Many pigments can be used: vegetable black, ultramarine blue, gold and silver bronzes, all give good results.

Abney's paprographic process is specially suitable for taking a number of copies from one tracing. Stout paper is floated for two minutes on—

Potass bichromate, .	13 grains.	30 grams.
Gelatine, . .	26 „	60 „
Water, . . .	1 ounce.	1000 „

It is hung up to dry and again floated, being this time hung up to dry in a position opposite to the first. Drying must take place in the dark.

After exposure the print is immersed in a dilute solution of alum to remove the greater part of the soluble chromate. It is then placed on a glass or zinc plate and surface moisture removed with blotting-paper. It is then inked with lithographic ink, applied with a soft leather or velvet roller, and soaked in water till all soluble chromate is removed. The design is left in black lines on a white ground. From this print forty to fifty copies can be taken in an ordinary copying press, the print being inked for each impression.

CHAPTER XVIII

Printing House Memoranda

To Oil Drawings on Paper for Printing.—

Castor-oil, ...	3 parts.
Alcohol, ...	10 „

Lay the paper face down on a glass plate and rub in the above solution with a small sponge. Warm before a stove to allow the oil to thoroughly soak in. When the paper has become transparent remove all superfluous oil into a clean rag or blotting-paper, and again warm. The paper can be restored to its original condition by soaking in alcohol once or twice, and then in water mixed with alcohol.

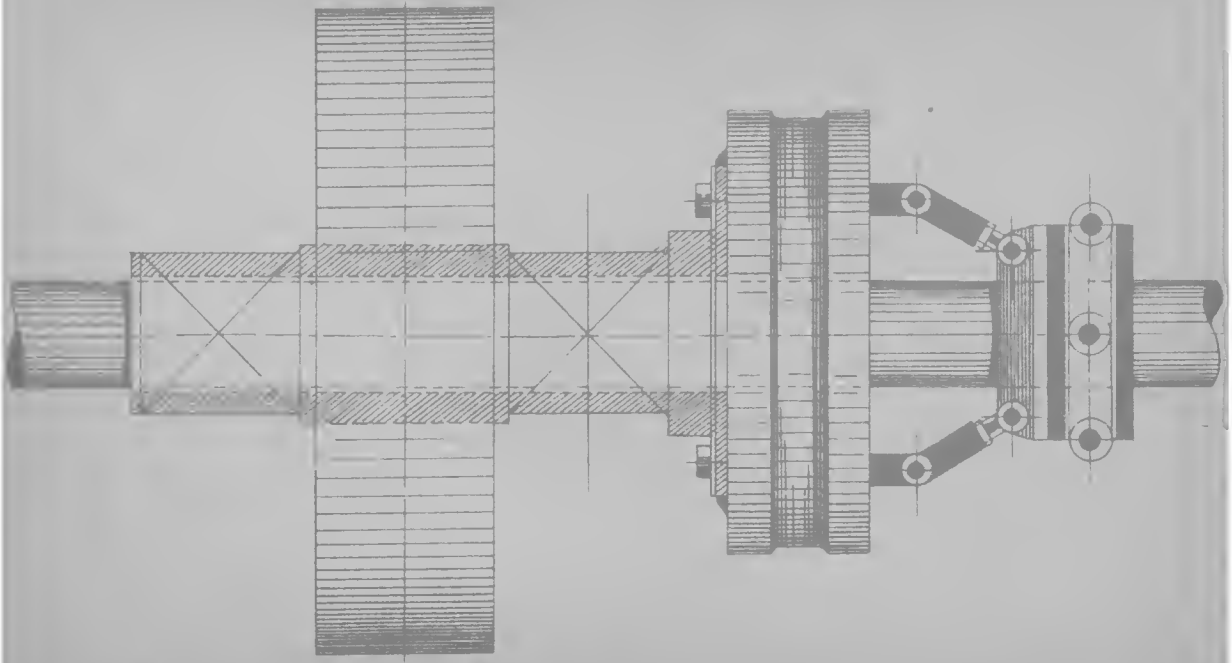
Another method is to iron paraffin wax into the warm and dry paper with a hot iron. Remove surplus wax by rubbing with a soft cloth.

Potash Oxalate Solution for Removing Stains.—

Potass oxalate,	1 part.	75 grains.	170 grams.
Water, .	6 parts.	1 ounce.	1000 c.cs.

This solution at once removes the blue image from both ferro-prussiate and Pellet prints. The paper should be afterwards well washed: if this is not done, the blue color is very liable to reappear in course of time.

Positive Copy reproduced from the preceding Negative Copy



For use on a pen the solution is thickened with a little gum-arabic, though, unless the draughtsman sends the copies back to the printing house to be again washed, he had better put in white lines on ferro-prussiate prints with Chinese white.

Mounting Prints.—To mount on linen, paste the back of the copy thoroughly well with fresh flour paste and leave for five or ten minutes. Tack the linen tightly to a smooth table and gently lower the pasted print upon it. Roll a duster round a piece of wood to make a firm but soft pad, and rub the paper into contact, working from the middle in all directions.

To Varnish Mounted Copies.—Give a coat of size (1 part of glue dissolved in 10 parts of water) and, when quite dry, varnish as evenly as possible with a good 'oak' or 'church' varnish.

Sizes of Drawing Papers.—

Demy, ...	17 × 22 inches.
Royal, ...	20 × 25 ,,
Cartridge, . .	21 × 26 ,,
Double crown, . .	20 × 30 ,,
Imperial, . . .	22 × 30 ,,
Double demy, .	22 × 35 ,,
Double elephant, . .	27 × 40 ,,
Antiquarian, . . .	31 × 53 ,,

CHAPTER XIX

Manipulation

Weights and Measures.—Since making up solutions enters very considerably into the working of the processes described in these pages, the question of weights and measures may be appropriately mentioned under this heading. In almost every instance, both metric and English units are given, but the writer earnestly advises the reader to work by the metric and to discard the English measures for evermore. A set of weights from 50 grams to 1 gram can be bought for one shilling and threepence. The fractional parts of the gram—·5, ·2, ·2, and ·1—can be cut out of aluminium foil, or a second set from 10 grams to ·01 gram only costs another eighteenpence. A 250 c.c. measuring cylinder costs about two and threepence, whilst a wide-mouth bottle of about 35 to 40 ounces capacity can be marked with a diamond for a litre measure, or a cylindrical litre measure bought for about five shillings.

The readiness with which large or small quantities of a solution can be at once compounded from the formula will convince the photographer of the superiority of the decimal over the English system.

Hydrometers.—When working on a large scale, particularly when chemicals (like ferric chloride) of

indefinite composition are being used, it is often advisable to adjust the strength of the solution by the hydrometer, as is done in the case of the Pellet sensitiser given on page 54. Hydrometers measure the specific gravity of the liquid, and are made to cover a certain range of specific gravity, say, 1·00–1·20, 1·20–1·40, and so on. They cost about half-a-crown each. The specific gravity of every liquid varies with the temperature, and it is therefore usual to adopt the temperature of 60° Fah. (15·5° C.) as that at which the gravity is to be taken. If the temperature of the solution differs more than a few degrees from this, the containing vessel is placed in warm or cold water, as required.

Baumé's hydrometer, which is much used on the Continent and in America, is differently graduated: its zero mark corresponds with the specific gravity of 1·00. The following figures give the gravities equivalent to degrees Baumé:—

Baumé.	Sp. Gr.	Baumé.	Sp. Gr.
30	1·256	40	1·375
31	1·267	41	1·388
32	1·278	42	1·401
33	1·289	43	1·414
34	1·300	44	1·428
35	1·312	45	1·442
36	1·324	46	1·456
37	1·337	47	1·470
38	1·349	48	1·485
39	1·361	49	1·500

Filtering.—Many of the solutions specified in these pages require filtering, if spotless results are to be obtained, and as many readers may never have fitted a filter paper into its funnel, perhaps one or two words on the right way to do this will not be considered out of place. A suitable filter paper is Rhenish, No. 597, made by Schleicher and Schüll, and obtainable at any chemical dealers in packets

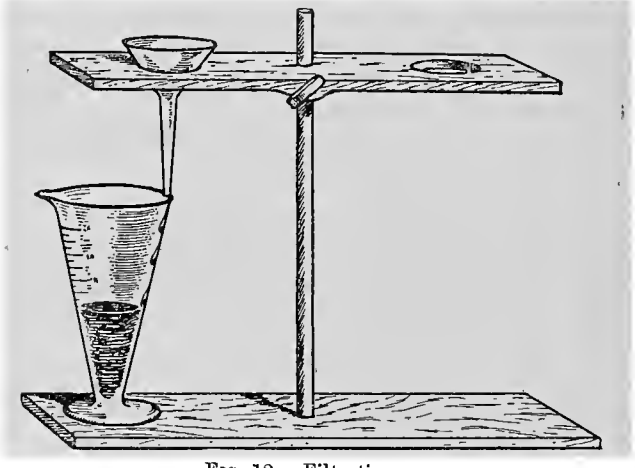


Fig. 12.—Filtration.

of 100 circular papers from 3 inches diameter upwards. The way in which the paper is fitted into the glass funnel has a good deal to do with the rapidity of filtration. First, fold the circular paper into two, and then again into four, making the last crease lightly. Place the paper in the dry funnel, and, gently placing the finger in the cone of the paper, see what amount of play is possible. The

filter ought to 'waggle' to and fro about a quarter of an inch. If the first folding does not give this, try again, laying down one edge of the semicircular paper a little short of the other and opening out the filter to form a cone of angle greater or less than 60°, as required. Place in the funnel, and press down the three-fold side of filter, so that the single thickness of paper is pushed against the glass on the opposite side and the point of the filter is turned away from

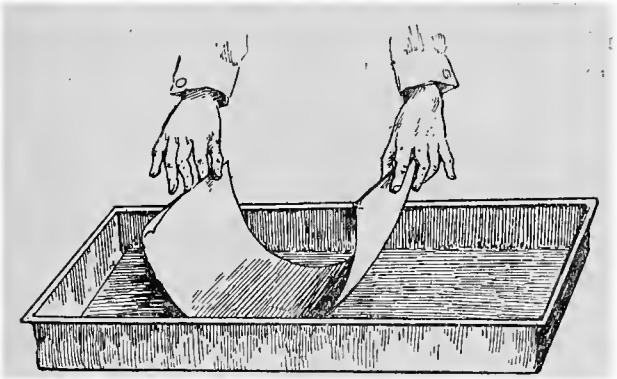


FIG. 13.—Coating Paper by Floating.

the three-fold side. Now, holding the funnel in the hand, single paper lowermost, pour water into the filter on the single side, bring into the vertical position and, taking hold of the two sides of the filter at the points where the single and treble thicknesses meet, slightly lift up the paper. The stem will at once fill with water and filtration will proceed rapidly. Though taking some time to describe, the operation only occupies a few seconds.

Coating Paper.—This is done either by floating on the solution or by brushing the solution over the paper. The latter method, inasmuch as it dispenses with large dishes and much solution, will commend itself to the photographer who only wants a small batch of paper. On the other hand, some solutions give a much more even coating by floating than by brushing.

(*a*) *By Flotation.*—To float the paper hold the sheet by opposite ends in a loop and gently lower the middle of the piece till it touches the surface of the liquid. By lowering the hands, the paper is gradually

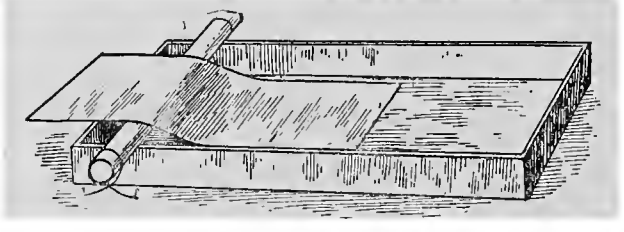


FIG. 14.—Withdrawing paper after Coating.

brought on to the surface of the liquid so as to expel air bubbles (fig. 13).

When withdrawing the paper, a good plan is to lay a piece of glass rod across one end of the dish and to slowly draw the paper over it. This removes superfluous liquid as well as covers any minute air bubbles left after flotation (fig. 14). The time of flotation varies with different papers and baths, and with the degree of impregnation desired. When one wants to keep the coating as much as possible on the surface of the paper, it is better to float for a short time, to

dry, and refloat, rather than to expose the paper to a more protracted flotation.

(*b*) *By Brushing.*—Soft camel's or badger hair brushes of good size are often used, but for many solutions the writer prefers a fine Turkish sponge or a piece of cotton wool, clean and free from grit. A Blanchard's brush is another convenient tool. A piece of glass plate about 6×3 inches has a strip of swansdown calico or Canton flannel folded over one end and secured with an elastic band (fig. 15).

After use, brushes and sponges should be well washed before being exposed to daylight. The cotton

FIG. 15.—Blanchard's Brush.

wool and the material in the Blanchard brush are used fresh each time.

When applying the sensitising solution, it is almost always necessary to keep the brush or sponge only just wet enough to give a thin coating. Too much liquid on the paper means a flat sunken image. Give the paper steady, even strokes in one direction and then crosswise. Streaks must, of course, be avoided as much as possible, but it is not at all difficult to coat paper with satisfactory uniformity.

Drying in a proper manner is important. It should be quick, but the paper must not get hot, or fogged images may result. Some papers can be dried at a short distance from a fire, but it is more satis-

factory to use a drying oven. This need not be at all an elaborate or expensive affair (for work on a small scale), and below are given the figure and description of one, which the writer constructed on the lines of one described by Mr Alexander Cowan in the *Photographic Year Book* for 1881.

A box of suitable size is made, and a central aperture about $2\frac{1}{2}$ inches diameter made in top and bottom. The upper aperture carries a length of stove piping in which, at about one foot above the box, a small Bunsen burner is fixed. A $\frac{3}{8}$-inch Fletcher's burner (price sevenpence without stand) answers well, and is screwed into a right-angled piece of tube, passing through the pipe. A small shutter is made in the pipe alongside the burner, for conveniently lighting the latter. To the lower aperture an inverted funnel-shaped vessel is attached, made of tin-plate and fixed by a flange to the under side of the box. From the side of this vessel a short length of stove pipe projects. The funnel is filled with fragments of asbestos, as used in gas fires. The interior of the box is provided with shelves of wood frames, covered with linen, on which the sensitive papers are laid to dry. These shelves are removable, and, if desired, the paper can be suspended to dry, by pinning it to a cross-piece of soft wood (about half-inch square section) and laying this on the supports of the top shelf. A hinged or sliding door is fixed to the front, and the whole is supported on four light iron legs, so as to leave the base of the funnel about twelve inches above the floor. An oil stove placed immediately below warms the air passing through the chamber containing the asbestos,

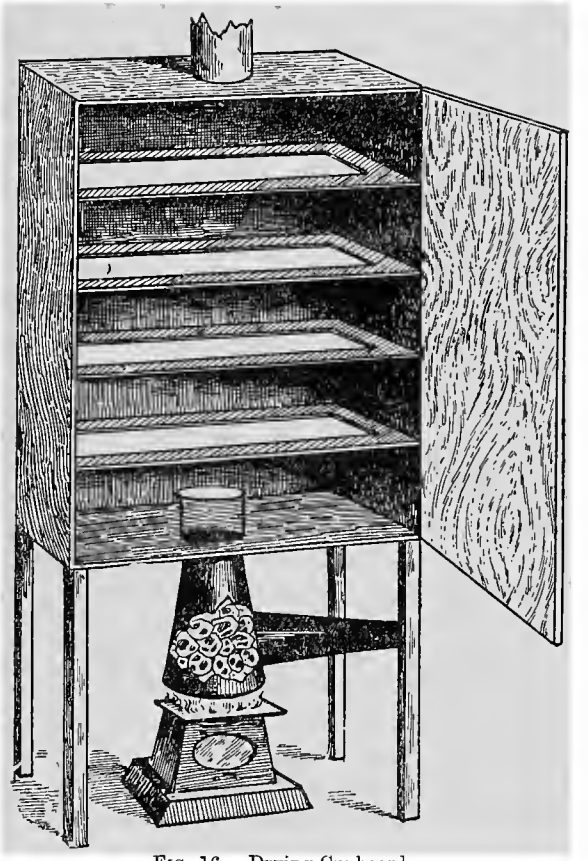


FIG. 16.—Drying Cupboard.

whilst the draught is increased by the burner in the chimney.

The use of this latter alone enables a current of cold air to be drawn through the apparatus. A very moderate increase in the temperature of the air is sufficient to make paper, coated by flotation or brushing, bone dry in half an hour.

Storage.—While the best results with almost all the processes here described are obtained on freshly prepared paper, it is often necessary to store it. Damp is the enemy of these papers, and, if they are to keep well, it must be excluded. A calcium chloride tube is the best receptacle, though it need not necessarily be of the form sold by the photographic dealers. Many household commodities are supplied in tins with almost hermetically sealing lids, and it is only necessary to divide off a small portion of the interior (to hold the calcium chloride) to have an efficient storage box.

To use calcium chloride to the best advantage it is mixed with asbestos. Soak commercial asbestos in a strong solution of the chloride, make the pasty mixture into little pats, and dry on the moderately warm part of the top of the stove. Gradually move to a hotter part, till the pats are dry right through, and store in a stoppered bottle for use. When these balls become damp they have only to be reheated on the stove to fit them for use again.

CHAPTER XX

Paper and Sizing

One of the advantages of the processes described in these pages is the facility with which the sensitising solutions can be applied to all kinds of papers, so that quite a variety of differently surfaced and tinted papers are placed at the photographer's disposal for printing purposes. The ferro-prussiate process can be worked with much commoner kinds of paper than others, such as kallitype; but among good-quality papers there is plenty of opportunity for the exercise of taste, and the newer school of pictorial photographers will no doubt find great possibilities in ringing the changes on tint of paper and color of image.

Among raw papers the well-known brands of Saxe and Rives, long used for albumenised paper, need no introduction to the student of photography. They are sold in sheets 18×22 inches, and can be used without additional sizing, though in almost every process a second sizing will do no harm, and will generally benefit the resulting paper as regards rapidity and brilliancy of image. Saxe and Rives paper can be obtained at some large photographic depôts, and as

the raw paper is not in very frequent demand it is as well to specify 'un-albumenised' when ordering it.

Whatman's drawing papers, supplied in three grades of surface, are very suitable both for large and small work. They are supplied in the various sizes used in drawing offices as given on page 97.

Some prices are here given as a guide to ordering:—

		Per sheet.		Per quire.	
		s.	*d.*	*s.*	*d.*
Demy, . . .	HP, N.	0	$1\frac{1}{2}$	3	0
Royal, . . .	HP, N.R.	0	3	6	0
Imperial, .	HP, N.R.	0	5	9	9
,, thick, .	HP, N.R.	0	$7\frac{1}{2}$	14	3
,, extra thick,	HP, N.R.	1	0	22	6
Double elephant, .	HP, N.R.	0	10	19	0

The letters in column 2 indicate the surfaces in which each size is made. HP, is hot pressed or smooth; N, not pressed or natural grain; R, rough.

Cartridge papers, too, are very suitable, and can be had in a variety of tones and sizes from large stationers such as George Gill & Sons, of Charterhouse Street.

Reeves & Son, and other artists' dealers, stock a few French drawing papers which are used for gum-bichromate work. The brands are, *Allonge*, *Canson* (18 different tints), *Michallet*, *Ingres* (5 tints), Of these *Michallet* and *Ingres* are papers of peculiar texture, and take the ferro-prussiate and kallitype solutions very well: with the other two brands the writer gets degraded lights, though possibly the pictorial worker may sometimes be able to make effective use of this property.

Other artists' papers which have been found suitable for photographic use are Wrigley's imperial amber antique rough-surface boards, Dutch hand-made *Van Gelder* (obtainable in several textures from the London agents, Grosvenor, Chater, & Co., Cannon Street, E.C.), and Japanese proof papers.*

Albumenised paper (unsensitised, of course) takes the ferro-prussiate and other solutions perfectly, and gives very fine brilliant prints.

Better-class hard-surface writing papers may be used. A local stationer or printer will supply these.

For engineering purposes, where large tracings are to be copied, it is imperative to use a stout paper. A common or thin paper means great risk of tearing the print during washing. Special tough, hard-surfaced papers are made for the purpose, in various degrees of stoutness—extra stout, stout, thin, and extra thin. The lighter kinds are suited for sending through the posts, or for making copies to be subsequently used as negatives (page 88). The heavier brands stand the wear and tear of shop use better. They are supplied in rolls of 30 inches wide and upwards. Steinbach (London agents, Otto König & Co.) makes good brands suitable for the various heliographic processes.

While very cheap papers can be employed for blue printing, if well sized and used fresh, it should be borne in mind that, for a sensitive paper to keep, sizing must be reduced to a minimum. Hence a pure, hard-surfaced, close-grained paper becomes necessary,

* E. Sanger Shepherd, *The Photogram*, 1896, p. 190 (Aug.).

if the coated paper is to be kept any length of time, but when it is convenient to use the paper within a few days of its being coated, it is quite easy to secure equally good results on much cheaper papers. Light-colored, heavy manilla wrapping paper, used for newspapers and magazines, can be used with this qualification.

Reeves & Son supply a fabric (*Linaura*) resembling tracing cloth which takes the ferro-prussiate solutions quite well. It is practically untearable and uninjured by moisture, whilst the sensitised fabric is said to keep in good condition for a much longer time than similarly coated paper. It is sold in rolls 36 inches and 42 inches wide.

Sizing fills up the pores of the paper, keeps the image on the surface, and so prevents flat and sunken prints. Besides this, the presence of the organic body —gum, starch, or gelatine—probably acts in many instances as a 'sensitiser' of the sensitive compound, thus conferring greater sensitiveness upon the paper.

The most effective and, for the amateur, most convenient method of sizing is with arrowroot as described by Duchochois.

Take—

Arrowroot, . .	9 grains.	20 grams.
Glucose, . .	2 „	5 „
Water, . . .	1 ounce.	1000 c.cs.

Mix the glucose and arrowroot with a little cold water, add the remainder hot, and boil up the whole in a porcelain dish. A cheap methylated spirit lamp

(fig. 17) is very convenient for this purpose, and will be found useful on many other occasions. An ordinary 'Granitine' developing dish can be used instead of the evaporating basin shown in the figure, though the latter is handier in use. Stir all the time heat is being applied, with a spoon or glass rod. As soon as the liquid boils extinguish the lamp and place the basin in a large dish of water to cool. Remove the skin from the surface, and strain through fine canvas.

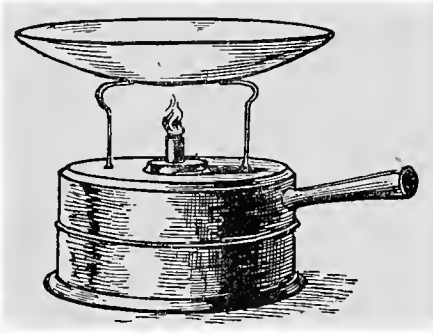


FIG. 17.—Spirit Lamp for making Size.

The necessary number of sheets of paper are nailed down by the four corners to a board about half an inch smaller each way than the paper. Obtain three soft Turkish sponges: rinse them in water: with one take up a little arrowroot solution, and, using it lengthways and crossways, spread the thin paste into an even layer. Then with the second sponge rub very lightly over the coating so as to spread it as evenly as possible. Take off any excess of paste with the third sponge.

Gelatine Sizing.—

Hard gelatine, .	150 grains.	9·5 grams.
Water, . .	30 ounces.	850 c.cs.
Alum, . .	45 grains.	3 grams.
Methylated spirit,	7 ounces.	200 c.cs.

Soak the gelatine in the water for half an hour, pour off the water into another vessel, and heat it in a water bath to 140° F. Then pour back over the gelatine, and when the latter is dissolved add the alum dissolved in a little water, and lastly the spirit; common methylated spirit precipitates mineral naphtha when mixed with water, so that, unless the unmineralised spirit can be used (and this is obtainable only in rather large quantities), absolute alcohol had better be substituted. Gently draw the paper into this solution, avoiding air-bells; soak for two or three minutes, dry quickly, re-immerse as before, and again dry, this time hanging up the paper by the two opposite corners.

Gum-arabic—a few grains per ounce—can also be used as size, and is brushed over the paper.

CHAPTER XXI

CHEMICALS

THE ferric salts are the compounds chiefly used in the processes described in these pages, and some space may therefore be devoted to the preparation and properties of these and several other equally important substances.

Ferric chloride may be purchased in three forms: (1) anhydrous (sublimed), (2) crystallised or solid, (3) in solution.

The anhydrous salt forms small dark green crystals, which absorb water from the air with the utmost readiness. Its cost is considerably greater than the other forms in which the salt is sold, but for use on a small scale it has the advantage of definitiveness of composition so long as it is kept well stoppered.

Crystal or solid ferric chloride is sold in large yellow lumps also very deliquescent. Their composition corresponds approximately to $Fe_2Cl_6.12H_2O$, equivalent to very nearly 60 per cent. of anhydrous chloride. Whenever 'ferric chloride' is prescribed in a formula without further specification, it may be taken that this crystal form is meant.

Solution of Ferric Chloride.—Ferric chloride is a most soluble salt, and solutions up to syrupy consistency can be prepared. A solution very much used in preparing heliographic papers has a specific gravity of 45° Baumé (=1·45, water=1). The ferric chloride liquor of the British Pharmacopœia (*liq. ferri perchloridi fortis*) has a specific gravity (1·42) very near this, and contains 286 grains anhydrous ferric chloride per ounce, or 653 grams per litre.

The following table, enlarged from *The Photogram*, 1894, page 139 (June), gives the gravities and strengths of ferric chloride solutions :—

Degrees Baumé.	Specific gravity.	Ferric chloride, anhydrous. Grams per 100 grams.	Ferric chloride, anhydrous. Grams per 100 c.cs.	Ferric chloride, cryst.* Grams per 100 c.cs.
48	1·501	49	74	127
45	1·454	47	68	118
43	1·426	45	64	111
40	1·384	41	57	98
38	1·359	39	53	91
36	1·334	37	48	85
33	1·298	34	44	76
30	1·264	31	39	68

Ferric ammonium citrate is purchased in thin, transparent scales of deep red color with a metallic-like lustre. It is soluble in half its weight in water

* Calculated on basis of 58 per cent. Fe_2Cl_6, as ascertained by analysis.

to a clear brown solution. If the crystals are opaque, and the salt forms a blue solution on first dissolving in water, decomposition has taken place, and such salt is liable to yield paper which will not give pure whites.

Preparation.—When circumstances make it advisable to prepare the salt, the simplest plan is to follow the instructions of the British Pharmacopœia.

Add 16 ounces (320 c.cs.) of strong ammonia (sold as ·880) to 40 ounces (800 c.cs.) of water. Add to this, little by little, 10 ounces (200 c.cs.) of ferric sulphate solution (B.P.) previously diluted with 40 ounces (800 c.cs.) of water. Stir well, and set aside for two hours, stirring occasionally. Filter on a calico or flannel filter, and wash the residual ferric hydrate with water till the washings give no more reaction for sulphate (on testing with a few drops of barium chloride solution) than the washing water itself. It would, of course, be better to wash in distilled water, but ordinary tap water will answer almost as well. Dissolve 4 ounces (80 grams) of citric acid in its own weight of water, and gently warm the solution on a water bath. Add the ferric hydrate (well drained) and stir together till nearly the whole of the hydrate has dissolved. Let the solution cool, add $5\frac{1}{2}$ ounces (110 c.cs.) of ammonia, and filter through flannel, adding a little distilled water, if filtration proceeds too slowly. Evaporate till syrupy, and dry on porcelain or glass plates at a temperature not above 100° Fah.

Ferric oxalate can be bought crystallised, but is expensive. It occurs in small, pale-bluish green crystals

which do not dissolve readily in cold water, but very readily in hot, without depositing when the solution cools. The salt and its solution should be kept in the dark.

Ferric oxalate is easily made from a ferrous or ferric salt, and the writer gives below the process and quantities of chemicals required for 100 grams of ferric oxalate in 20 per cent. solution. The reader who wishes to use English weights and measures must substitute for grams some English unit throughout—grains, drachms, or ounces, according to the quantity he requires.

Iron alum or ferric chloride solution are the simplest raw materials for the manufacture of ferric oxalate. If ferrous sulphate is used the following preliminary treatment is necessary.

150 grams (theory, 148) of protosulphate of iron are dissolved in hot water, a little sulphuric acid added, and then, very cautiously, about 15 c.cs. of strong nitric acid (sp. gr. 1·4). The liquid must be in a porcelain basin. Enamelled iron might, with some risk, be used. The first addition of the nitric acid produces a dark brown color. As the acid is added its action becomes more energetic, and at the end of the process (which may be thus recognised) the liquid bubbles up, giving off red fumes and becoming clear orange-red in color. A little more nitric acid is then added, and the liquid allowed to cool. From this stage the solution which contains ferric sulphate and nitrate is treated exactly as the iron alum or ferric chloride solution to be now described.

256 grams iron ammonium alum, or 132 c.cs. ferric chloride solution (B.P., sp. gr. 1·42), are diluted with water to about 1000 c.cs. and poured into 100 c.cs. strong ammonia diluted to a like amount. The alkaline liquid may be contained in a clean tin vessel. The precipitated ferric hydrate is allowed to settle, the clear liquid syphoned off, and some boiling water stirred up with the residual precipitate. The whole is then poured on to a flannel or calico filter (fig. 18)

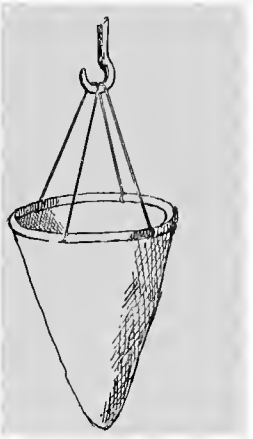


Fig. 18.—Filter for washing Ferric Hydrate.

and washed for several hours in a current of cold water, being occasionally well stirred up on the filter with a piece of glass rod, rounded at the end, or a silver spoon. As much as possible of the liquid is squeezed out of the flannel, and the precipitate scraped out with a silver spoon into a porcelain basin.

All the foregoing operations may be performed in

broad daylight. The remaining part of the process must be conducted in a dark room.

100·5 grams of finely powdered, pure oxalic acid are sprinkled over the precipitate, mixed up with it, the dish covered over and left to itself, save for occasional stirring, for a day or two. The process of solution may be hastened by heating to not above 85° Fah.: for this a small oil stove placed some distance below the dish answers well. Test the temperature with a thermometer: if it goes much above 85°–105° Fah., the salt is partly reduced to ferrous oxalate. The solution gradually turns from pure green, through yellowish-green, to greenish-brown. This strong solution must be diluted with distilled water till it measures 500 c.cs. 10 c.cs. then contain 2 grams: it will keep indefinitely in a cool and dark place.

Potassium ferrocyanide (yellow prussiate of potash) occurs in large lemon-yellow crystals, sometimes turbid or translucent (not a sign of impurity). The salt keeps well, exposed to light and air, has a neutral reaction, and is not poisonous. The saturated solution (at 60° Fah.) contains 259 grams per litre and has a specific gravity of 1·14.

Potassium ferricyanide (red prussiate of potash) forms fine, large, blood-red crystals which, when the salt is pure and fresh, are transparent. The powdered salt is orange-red. Exposed to light, both in the solid state and in solution, it is decomposed with formation of ferrocyanide and of a blue precipitate. It is therefore very important to store the solution (well stoppered) in the dark and to rinse crystals, which are not clear ruby red, with a little water—

drying them between blotting-paper—before weighing them. The concentrated solution is brownish-yellow; the weak, lemon-yellow. 100 parts of water dissolve nearly 40 parts of the salt at ordinary temperature.

Gallic acid ought to be nearly white needles, but is often of a brownish tinge. One part dissolves in 100 parts of cold water, 3 parts of boiling water, 12 of glycerine, and 5 of alcohol.

Tannic Acid.—Light brownish powder of thin glittering scales. It is very soluble in water, alcohol, or glycerine. One part of either of these solvents dissolves one part of the acid.

Gum-arabic is nearly colorless, but often has a yellowish tint: it should be nearly inodorous. It is insoluble in alcohol and very soluble in water, forming a translucent viscid solution, which is thickened or rendered turbid by ferric salts. The price of gum-arabic varies from two shillings to four shillings and sixpence per pound, according to its purity. One of the best brands is 'White Senaar,' another 'Senegal.'

CHAPTER XXII

Chemistry

Ferrous and Ferric Salts.—There are two series of salts of iron—the ferrous and the ferric. They differ in the proportion of oxygen (or other negative element, such as chlorine) which they contain. Ferrous chloride, $FeCl_2$, may be taken as typical of the ferrous series, and ferric chloride, Fe_2Cl_6, of the ferric series. It is quite easy, by chemical means, to convert any one member of one series into the corresponding member of the other. Thus, reducing agents, substances which readily combine with (and remove from any compound) oxygen, chlorine, or similar electro-negative elements, like sulphurous acid, convert ferric salts into ferrous; whilst oxidising agents, substances like nitric acid or potassium permanganate, which readily supply oxygen, chlorine, or similar elements to any compound, convert ferrous salts into ferric salts.

Chemical and Photo-chemical Reduction of Ferric Salts.—The above chemical reactions go on irrespective of the action of light, though heat is sometimes necessary to start or complete them. There are, however, certain reducing agents which convert ferric into ferrous

salts only under the influence of light. For instance, a solution of ferric chloride in ether remains quite unaltered in the dark, but on exposure to sunshine soon loses its yellow color and becomes reduced to ferrous chloride, the change being accompanied by the decomposition of a portion of the ether.

Paper, too, saturated with a solution of ferric chloride and dried, is similarly capable of effecting the reduction of the ferric salt. These changes—not merely chemical, but photo-chemical—are examples of many which take place, not in the case of salts of iron only, but of compounds of uranium, cobalt, manganese, chromium, and other metals.

There is one distinguishing feature common to the bodies which undergo photo-chemical decomposition in this way—or at any rate to those of which any practical use can be made. They are all compounds of elements which, like iron, are capable of existing in two states of oxidation. It is generally only the more highly oxidised compounds which are sensitive to light, the decomposition resulting in the formation of a salt of a lower degree of oxidation, and in order that photo-chemical action shall take place, it is necessary that the metallic salt shall be associated with a mild reducing agent such that, when exposed to light, the reduction of the ferric (or other) salt and the oxidation of the reducer shall go on together.

If the reducer is too powerful, decomposition takes place without the aid of light at all (ferric chloride and sulphurous acid): if no compound is present, which can take up the oxygen or other element from

the compound exposed to light, no photo-decomposition takes place (ferric chloride in aqueous solution): whilst the case of ferric chloride in ethereal solution is an example of the principle just cited, of exposing a substance in the presence of a second, capable of promoting its decomposition in the light.*

This reducing matter need not necessarily be a separate compound: it may be combined with the ferric salt, as when organic salts of iron (oxalate or citrate) are made use of.

The chief compounds of which practical use has been made are the ferric and uranic salts and the alkaline dichromates, and the processes which have been developed depend on the differences in the behaviour of various reagents towards these salts and their lower compounds. For example, ferrous salts reduce the noble metal from compounds of platinum or silver, whilst no such action is exerted by the ferric salts—a difference which is the basis of the platinotype and kallitype processes.

Action of Light. Ferric Salts.—The ferric salts of mineral acids (such as sulphuric, hydrochloric) are reduced to the corresponding ferrous salts when exposed to light with various organic bodies, such as oxalic acid, citric acid, tartaric acid, gelatine, gum, etc., whilst a similar change takes place in the case of organic salts of iron like the oxalate, tartrate, and citrate. Very often the use of a double salt of iron and ammonia gives better results, and the reason ascribed is that the ferric salt possesses the property

* *Vide Chemistry of Photography*, by Raphael Meldola, Macmillan, 1891, pp. 12–20 and 71–82.

of dissolving the newly formed ferrous salt to such an extent as to weaken the vigour of the image. The introduction of ammonia into the compound counteracts this solvent action, and hence ferric ammonium citrate, ferric ammonium oxalate, etc., are compounds which are very frequently used in preference to the simple iron salts.

Uranium Salts.—The metal uranium forms two series of salts—the uranic (yellow solutions) and uranous (green solutions). The salts most used are uranic nitrate, chloride, and acetate, though the organic salts of uranium offer a promising field for experiments. On exposure to light, uranous oxide, UO_2, and the uranous salt of the acid are generally produced.*

Chromium Compounds.—Exposed to light in contact with organic substances such as gum, gelatine, etc., alkaline dichromates ($K_2Cr_2O_7$) become reduced to chromium salts, whilst the associated organic matter has several of its physical properties modified. Both of these changes are utilised in one process or another for the production of an image.

Thus, the unaltered chromate reacts with silver nitrate, giving a red precipitate of silver chromate, whilst the reduced chromium salt does not; but the most important processes are those dependent on the alteration of the gum or gelatine. The principal changes are in (1) solubility, (2) hygroscopic properties, (3) power of imbibition (or ability to absorb water).

* *Vide* Burnett's "Researches," *British Journal of Photography*, 1857 and following years.

(1) Gelatine or gum, mixed with bichromate, becomes insoluble in hot water, a change which is the basis of the well-known carbon and similar processes.

(2) Bichromated gum or dextrine is tacky before exposure to light, but after isolation is found to have lost this property, so that a fine powder does not adhere to the exposed portions (*anthrakotype* and other 'powder' processes).

(3) Bichromated gelatine, exposed to light, loses its power of swelling by absorption of water, and if a gelatine surface, some parts of which have been exposed and others not, be immersed in cold water and a roller, charged with greasy ink, then passed over it, the ink is repelled from the unexposed portions, but adheres to the unswollen portions (basis of *paprotype*, page 95, *heliotype*, and other processes).

As explained above, all these printing processes with metallic salts—to use a long phrase for what the Germans call *Lichtpausverfahren*—depend on the difference in action of certain reagents on the salts and on their products when exposed to light.

The principal reagents are potassium ferrocyanide, potassium ferricyanide, gallic and tannic acids, and silver nitrate. By referring to the reactions given below, the student will be able to understand the theory of the processes described in these papers.

Potassium Ferrocyanide. *Ferric Salts.*—Deep blue precipitate of Prussian blue.

$$3K_4Fe(CN)_6 + Fe_2Cl_6 = 3Fe(CN)_2.2Fe_2(CN)_6 + 12KCl.$$

Ferrous Salts.—Bluish-white precipitate, which rapidly becomes blue on exposure to the air.

$$K_4Fe(CN)_6 + FeSO_4 = K_2Fe.Fe(CN)_6 + K_2SO_4.$$

Uranic Salts.—Red-brown precipitate.

Uranous Salts.—Red-brown precipitate.

Potass Ferricyanide. *Ferric Salts.*—No precipitate: merely a brown coloration.

Ferrous Salts.—Deep blue precipitate of Turnbull's blue, $Fe_3.Fe_2(CN)_{12}$.

Uranic Salts.—No precipitate.

Uranous Salts.—Red-brown precipitate of uranous ferricyanide.

Tannic Acid. *Ferric Salts.*—Intense bluish-black precipitate.

Ferrous Salts.—In strong solutions, a white gelatinous precipitate: none in weak solutions.

Uranic Salts.—?

Uranous Salts.—Red-brown precipitate.

Silver Nitrate. *Ferric Salts.*—No reaction.

Ferrous Salts.—Precipitate of metallic silver.

Uranic Salts.—No reaction.

Uranous Salts.—Precipitate of metallic silver.

Alkaline Chromate.—Red precipitate of silver chromate.

Chemistry of Prussian Blue.—It would be out of the scope of this work to discuss the chemical constitution of the several varieties of Prussian blue. The

student should refer to an article by W. Dittmar,* where the chemistry of the question is discussed. But some of the chemical and physical qualities of these blues are of practical importance from the present point of view.

On exposure to bright light, Prussian blue fades a little, and regains its original intensity of color in the dark.

Caustic and carbonated alkalies (caustic soda and washing soda) decompose it, separating a hydrated oxide of iron and forming a soluble ferrocyanide—

$$Fe_3.Fe_2(CN)_{12} + 8KOH = 2K_4Fe(CN)_6 + Fe_3O_4.4H_2O.$$

The same result is produced, though much more slowly, by solutions of carbonate of lime and of magnesia, and as these salts are the almost invariable constituents of ordinary drinking waters, the point is of practical importance. If washed too long, the blue image is very considerably weakened.

Silver nitrate and mercuric sulphate act very powerfully on Prussian blue, destroying the blue color: the latter salt forms cyanide of mercury and sulphate of iron.

Oxalate of potash immediately decolorises and dissolves Prussian blue.

* Thorpe's *Dictionary of Applied Chemistry*, vol. i. p. 640.

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INDEX

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