PHOTOGRAPHERS' FORMULARY

PHOTOGRAPHERS' FORMULARY KALLITYPE PRINTING KIT

Kallitype printing is similar to platinum and palladium printing in theory and technique. However, the Kallitype printing process uses the less expensive silver salt in place of platinum or palladium salts. Good Kallitypes have a platinum-like quality. Print color can be controlled by development. Sufficient chemicals for black, brown, or sepia development are included in this kit.

CHEMICALS CONTAINED IN THIS KIT

This kit contains the following chemicals:

Chemical	Amount
Arrowroot starch	20 g
Ferric oxalate	30 ml
Silver nitrate	2 g
Rochelle salt	100 g
Borax	75 g
Potassium oxalate	60 g
Sodium thiosulfate, pentahydrate	50 g
Ammonia (28%)	15 ml
Potassium dichromate	5 g

CHEMICAL SAFETY

PLEASE USE DISTILLED WATER FOR ALL SOLUTIONS

All chemicals are dangerous and must be treated with respect. Please read the chemical warning one each package of chemical. **Consult with local sewer and water authorities regarding proper disposal of darkroom chemicals in your area.**

There are four chemicals in this kit that need special attention: silver nitrate, potassium oxalate, ammonia, and potassium dichromate. A separate discussion of the safety and characteristics of ferric oxalate fellows this section.

Silver Nitrate is both an oxidizer (fire hazard) and a caustic (can cause skin burns). Clean up any spilled solid silver nitrate with water and dispose of any excess down the drain. Never dispose of solid silver nitrate in a wastepaper basket.

If solid silver nitrate comes into contact with the skin, a chemical burn may result. Wash the area with cold water followed by soap and water. Treat a chemical burn in the same manner you would a heat burn.

When dilute solutions of silver nitrate are spilled on the skin, a brown to brown-black stain results. The color is due to silver metal bound to the protein of the skin and cannot be washed off. While there are chemical methods for removing the brown stains, the best procedure is to just let them wear off.

Potassium Oxalate: is an anticoagulant (prevents blood clotting) and a poison. Since this chemical is used as the clearing bath, it can easily come into contact with your skin. It is strongly advised that you use tongs to clear Kallitype prints or wear rubber gloves if you feel you need to handle the prints

during clearing. Should potassium oxalate solution come into contact with your skin, wash immediately with soap and water.

Ammonia (28%): Concentrated ammonia is also called ammonium hydroxide. This liquid releases extremely choking ammonia gas when opened. NEVER SNIFF THE LIQUID. Always keep any container with a solution of ammonia well capped. In the Kallitype process, ammonia is used in the fixing bath. Mix this bath in a well-ventilated area.

Potassium dichromate is both toxic and an oxidizer (potential fire hazard). To dispose of excess solid potassium dichromate, always wash the solid down a drain with copious amounts of water. Never dispose of the solid in a wastepaper basket.

Spillage of a dichromate solution on the skin will cause a chemical burn, which will appear as ulceration. In addition, all chromium compounds are potential carcinogens. We strongly advise you to use disposable rubber gloves when handling this compound or its solutions. Clean all trays and containers thoroughly with water, followed by soap and water. Dispose of excess dichromate salts and their solutions down a drain with large a volume of water.

Ferric Oxalate

The photographic term "ferric oxalate" is a misnomer, which has given rise to a considerable amount of confusion in the photographic literature. There are two common forms of this compound: tri-potassium ferric oxalate [$K_3Fe(C_20_4)_3$] and tri-hydrogen ferric oxalate [$H_3Fe(C_20_4)_3$]. While both forms are photosensitive, only the acidic form is sufficiently photosensitive to be useful in photography.

The original formulas for Kallitype printing call for dissolving solid ferric oxalate with an excess of oxalic acid. With the original directions, it is not clear which of the two forms of ferric oxalate are to he used. Solid tri-potassium ferric oxalate is a tri-hydrate that is thermally stable up to 110°C/125°F and stable in the dark for extended periods of time. The solid can be used in subdued room light; however, the solid is destroyed (turns from green to brown) when exposed to ultraviolet light. Tri-potassium ferric oxalate is photo-activated by placing it in an acid solution, where it is converted to the tri-hydrogen form. Photographers' Formulary does not recommend the use of the green, solid tri-potassium ferric oxalate for Kallitype printing. Its photo-activity is low and it is difficult to convert to the more active form.

The ferric oxalate supplied with your kit is a 20% solution of tri-hydrogen ferric oxalate. This chemical is prepared by Photographers' Formulary by the iron alum-oxalic acid procedure and contains a slight excess of oxalic acid.

Tri-hydrogen ferric oxalate is photosensitive to light in the 460-nm region. As a photosensitive material, ferric oxalate is very slow when compared with silver-grain emulsions. However, ferric oxalate should still be used in a darkroom with a red safety light. Tri-hydrogen ferric oxalate is probably heat-sensitive, but the exact extent is not known. To be on the safe side, do not heat the solution (or the sensitized paper when it is being dried) over 50°C/122°F. Tri-hydrogen ferric oxalate is very water-soluble and its solution has a yellow to yellow-green appearance when first taken into room light.

Chemical Test for Photo-activity and Excess Ferrous Ions in Ferric Oxalate

In a suitable glass container (a test tube or a whiskey shot glass), place about 2 crystals of potassium ferricyanide (Catalog number 10-1010) and about 2 ml of water. Stir until the solid has dissolved. In

the darkroom under a red safety light, add 1 drop of ferric oxalate. Hold the test container up to the red light in such a way that you can see through it as you add the drop of ferric oxalate.

If the ferric oxalate does not contain excess ferrous ions, you will observe only a slight darkening of the solution. If excess ferrous ions are present, the test mixture will turn very dark or black. (It actually turns blue.)

Step out of the darkroom and quickly look at the test container. The solution should appear yellow-brown to orange. If a trace of ferrous ions is present, it will appear green. It may have a blue cast - the deeper the blue, the poorer the quality of the ferric oxalate.

Hold the test container up to the side of a 100-watt frosted light bulb. Within a minute you should see a deep blue coloration forming on the side of the test container nearest to the light bulb. The formation of the deep blue color indicates that there is photosensitive ferric oxalate present. This blue color is due to Prussian blue, which is formed by a reaction between the newly formed ferrous ions and the ferricyanide ion.

With a little practice using exposed and unexposed solutions of ferric oxalate, you will be able to gauge the quality of the ferric oxalate before you mix it with an expensive metal salt.

MIXING THE SOLUTIONS

The Sensitizer

Chemical	Amount
Ferric oxalate, 20%	30 ml
Silver nitrate	2 g

In a darkroom using a red safety light, add the solid silver nitrate to the ferric oxalate solution. Stir the resulting mixture with a glass or plastic rod to dissolve the solid. It is very common for a precipitate of silver oxalate to form. This precipitate does no harm. If your sensitizer does form a precipitate, just be sure you do not transfer it to the paper you will be coating.

The sensitizer must ripen for a few (2-3) days before use. Keep the solution in the darkroom and stir or mix it occasionally. The mixing is especially important if a precipitate formed during mixing.

The Developer Stock Solutions

Two stock solutions (called A and B) are to be prepared. With these two stock solutions, three types of developers can be mixed: a back-tone developer; a brown-tone developer; and a sepia-tone developer. The proportions of Stock Developer Solutions A and B needed for these three developers is described in the section on "Development".

Stock Developer Solution A

Chemical	Amount
Distilled water (52°C/125°F)	200 ml
Rochelle salts*	100 g

*Also called Potassium Sodium Tartrate

Place the hot water in a mixing bowl, add the solid, and stir. Rochelle salts dissolve with absorption of heat: therefore, the solution will cool and it may be necessary to warm the bowl slightly. Upon stirring, the mixture turns cloudy but, in time, will clear. When the solid has completely dissolved, transfer the solution to any convenient storage container.

Stock developer solution B

Chemical	Amount
Distilled water (52°C/125°F)	400 ml
Borax	75 g

Mix this solution in the same manner as Stock Solution A. The borax will dissolve slowly, and it is not uncommon for residual solid to remain in the container.

Clearing Bath

Chemical	Amount
Distilled water (20°C/68°F)	500 ml
Potassium Oxalate	60 g

Place the water in a mixing bowl and add the solid. Stir the mixture until the solid goes into solution, store in any convenient pint size container.

Since potassium oxalate is rather toxic, we suggest you mix this solution in a sink and, after mixing, clean all the mixing utensils thoroughly with water before they are removed from the sink. We also recommend that you wear rubber gloves while preparing this solution.

Fixing Bath

USE DISTILLED WATER

Chemical	Amount
Distilled water (52°C/125°F) Sodium thiosulfate, pentahydrate	1000 ml 50 g
Ammonia, 28%	12 ml

Place the warm water in a mixing bowl, add the solid sodium thiosulfate, and stir the solution until the solid goes into solution.

Your kit will have a bottle containing approximately 12 ml of 28% ammonia. In a well-ventilated area, add the liquid to the sodium thiosulfate solution. Stir the resulting mixture to insure it is homogeneous, store in any convenient liter size container.

10% Potassium Dichromate Solution for Contrast Control

Chemical	Amount
Distilled water (52°C/125°F)	50 ml
Potassium dichromate	5 g

Place the water in a mixing bowl and add the solid. Stir the mixture with a glass or plastic rod until the solid goes into solution. Store the solution in a bottle with plastic cap. (Do not use a metal cap; the dichromate will corrode it.)

Since potassium dichromate is toxic, we recommend that you mix this solution in a sink and, after mixing, wash all the utensils before removing them from the sink. We strongly recommend that you wear rubber gloves when mixing and handling this solution.

Paper

Almost any paper can be used. However, the final impact of the print is dependent upon the type of paper, the extent of sizing, and the type of sizing that you use. You will have to experiment with different papers and sizing to obtain the effect you wish. We suggest you start with Crane's Kid Finish (Platinotype) 90 lb.

Sizing

The extent of sizing will determine the porosity of the paper and thus the degree to which the image will be embedded in the fibers of the paper. You may not wish to use any sizing at all.

Arrowroot starch is included in your kit should you wish to size your paper. However, you may wish to select a different sizing material because the sizing material will affect the final color of the print. Prints made with arrowroot starch-sized-paper will have a brown color while those sized with gelatin (Catalog number 10-0590) will have a blue tone.

Sizing the Paper

Preparation of Sizing Solution: Your kit contains 20 g of arrowroot starch. Place this starch in a 1-liter container that you can heat (such as a sauce pan) and add a small amount of hot water (about 20 ml). Stir the mixture into a thick cream. Be sure that no lumps remain. Add 1 liter of hot water with constant stirring. Boil the mixture for 5 minutes, and then let it cool to room temperature. Skim off any scum or decant the clear solution into a storage container.

Application of the Sizing Solution: Pin the paper to a board and apply the sizing solution to the surface with a clean brush. Brush the solution onto the paper, first across, then up and down, until the paper is completely wet. Using another brush (like a clean shaving cream brush), work the surface until it loses its gross. Allow the paper to dry, either hung or still pinned to the board.

The Negative

The Kallitype process is a contact print process; therefore you will need a negative the same size as the size of the print you wish. Kallitype is capable of an extremely long tonal range. Negatives with a density range up to 1.85 can be used. The final print contrast can be, to some extent, be increased by adding potassium dichromate to the developer (not the sensitizer; see "Development" below).

Sensitizing the Paper:

Using a good brush and working in very subdued light or in a darkroom under a red safety light, brush the sensitizer solution onto the paper pinned to a board. The brush strokes should be from top to bottom and from side to side. It is not necessary to measure the amount of sensitizer used.

The amount of sensitizer needed will depend upon the porosity of the paper. In general you can expect to use about 1 ml for a 4-by-5 print (4 ml for an 8-by-10). Since this kit contains 30 ml of ferric oxalate which was used to make the sensitizer solution, you can expect to be able to make up to 30 4-by-5 prints (or about seven 8-by-10 prints).

Allow the sensitized paper to dry in the dark. The drying of the print can be speeded-up by using a hand-held hair dryer. DO NOT OVER HEAT THE PRINT.

Exposure

Ferric oxalate absorbs in the ultraviolet region of the spectrum. Therefore you will either have to use sunlight or a sunlamp. (An enlarger will not work.) It is difficult to obtain consistent results with sunlight. Therefore, we recommend that you use a sunlamp; a General Electric 275- or 300-watt bulb is satisfactory.

Glass absorbs ultraviolet light: therefore, it is best to contact print without a frame if at all possible. In the darkroom, tack the sensitized paper to a board, position the negative on it, and pin it down. Place the board directly beneath a sunlamp (12-18" away). The lamp generates considerable heat; therefore, do not place the lamp too close to the negative.

Ferric oxalate is extremely slow. Exposure will take 10-20 minutes. It is advisable to run a test strip to calibrate your equipment setup.

Development

Formulas for three different developers are described below. You may wish to experiment with intermediate mixtures of your own. In general, if you increase the amount or proportion of Stock Developer Solution A (Rochelle salts) in the developer, you will increase the sepia-tone of the print. If you increase the amount or proportion of Stock Developer Solution B (borax), you will increase the blackness of the print.

Print contrast of any of these developers can he increased by adding 5 to 20 drops of 10% potassium dichromate solution per 500 ml of the mixed developer.

For Black-tone Development

Chemical	Amount
Distilled water (20°F/68°F)	200 ml
Stock Developer Solution A	72 ml
Stock Developer Solution B	128 ml
Distilled water to make	500 ml

Place 200 ml of water in a mixing bowl (or development tray) and add both stock developer solutions. Add 100 ml of water to bring the final volume up to 500 ml. Stir the solution to ensure the solution is homogeneous. Store the mixed developer in any convenient container.

Develop for 5 minutes. This developer works best if it is warm, (around 38°C/100°F or higher).

For Brown-tone Development

Chemical	Amount
Distilled water (20°F/68°F)	200 ml
Stock Developer Solution A	96 ml
Stock Developer Solution B	64 ml

Distilled water to make	500 ml

Mix this developer in the same manner as was described for the Black-tone Developer except use 140 ml of water to bring the final volume up to 500 ml.

Develop for 5 minutes. Like the black-tone development solution, this developer works best if it is warm.

For Sepia-tone Development

Chemical	Amount
Distilled water (20°F/68°F)	200 ml
Stock Developer Solution A	48 ml
Distilled water to make	500 ml

Mix the water and the stock developer solution in a mixing bowl (Or development tray) and add sufficient water (252 ml) to bring the final volume up to 500 ml. Store the mixed developer in any convenient container. Develop 10 minutes at room temperature.

Final Steps

The final clearing, fixing and washing will determine the quality of the final print. For the print to be stable, the iron salt, the excess silver salt, and all the thiosulfate (used to remove the silver salt) must be removed.

Clearing: Soak the print in the potassium oxalate clearing-bath for 5 minutes at 20°C/68°F. Drain the solution from the print, give it a quick water rinse, and then transfer it to the thiosulfate fixing solution.

Fixing Soak: Soak the print for not more than 5 minutes in the sodium thiosulfate fixing bath, a longer soak will cause the print to fade. Do not use a standard photographic fixing bath; the finely divided, unprotected silver metal will be etched from the print.

Final Water Wash:. The thiosulfate just introduced must he completely removed to ensure print stability. Wash the print for 40 minutes in running water (20°C/68°F). A more effective procedure is to wash the print in running water for 2-4 minutes to remove the bulk of the thiosulfate, then use Hypo-Clear (cat. no. 03-0165), followed by a 15-20 minute water wash.