# Formulary

#### PHOTOGRAPHERS' FORMULARY NEW 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.

#### 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
Sodium Citrate	300 g
Citric Acid	150 g
Sodium thiosulfate, pentahydrate	2 packets of 50 g

#### PLEASE USE DISTILLED WATER FOR ALL SOLUTIONS

#### **CHEMICAL SAFETY**

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

This kit contains silver nitrate; a chemical that needs special attention. A separate discussion of the safety and characteristics of ferric oxalate also follows in 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 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.

#### 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  $[K_3Fe(C_2O_4)_3]$  and tri-hydrogen ferric oxalate  $[H_3Fe(C_2O_4)_3]$ . While both forms are photosensitive, only the acidic form is sufficiently photosensitive to be useful in photographic processes.

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 best to be 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 or Kodak OC 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 incandescent 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 if observed under incandescent light.)

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 - USE DISTILLED WATER FOR ALL SOLUTIONS

<u>The Sensitizer</u>

Chemical	Amount
Ferric oxalate, 20%	30 ml
Silver nitrate (to make a 10% Solution)	2 g
Distilled water (Warmed to 120°F)	20 ml

Under a red safelight or under indirect and low level incandescent lighting stir in the silver nitrate to 20 ml of warm distilled water. See Final Notes & Suggestions at the end for advice

on how to best mix the small quantity of silver nitrate solution. The silver nitrate does not dissolve readily and may contain small grains of material suspended in the solution. Stir the solution to dissolve as much of the material as possible. It will eventually completely dissolve but the solution can be useable shortly after mixing. Pour the dissolved silver nitrate solution in the small container provided. The ferric oxalate and silver nitrate solutions will be combined just before coating the paper to form the Kallitype sensitizer.

# **Developer Solution**

Chemical	Amount
Distilled water (52°C/125°F)	1500 ml
Sodium Citrate (to make a 10% Solution)	300 g

The developer is a 20% solution of sodium citrate. In a suitable mixing container slowly stir in the contents of the 300 g packet of sodium citrate to 1100 ml of distilled water. Stir until completely or almost completely dissolved. Then add additional distilled water to make 1.5 liters (1500ml). Continue to stir until the powder is completely dissolved. Pour contents into a 1 liter container and the remainder into a 500 ml container.

The sodium citrate in the 500 ml container is added as needed to the developer in 100 ml increments as a replenisher. After developing the equivalent of approximately four 8x10 prints add 100ml to the existing developer in the tray. Then continue to add an additional 100 ml each time you have developed the equivalent of two 8x10 photos. Save the contents of the developer after each printing session for reuse and discard after the contents of the kit have been used up. You may also manage your developer solution by starting with a lesser amount and discard it after a few prints. As the developer becomes clouded with the byproducts of development pour all or part of the used developer out and replace it as needed.

## **Clearing Bath**

Chemical	Amount
Distilled water (20°C/68°F)	5000 ml
Citric Acid (to make a 3% Solution)	150 g

The photographer may mix this solution to use as needed in a 3% solution, 30 grams per liter or mix it all ahead of time. In this case you will need storage for 5 liters of solution. In a mixing container add the 150 g of citric acid to 4 liters of distilled water. After the citric acid has dissolved add distilled water to reach a final volume of 5 liters.

# **Fixing Bath**

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

In a suitable mixing container add 50 grams of sodium thiosulfate to 1 liter of distilled water. Stir until all solids have gone into solution. Sodium thiosulfate does not have an extended shelf life once mixed with water so your kit contains two packets of this substance. Each packet is adequate to fix 4-5 8x10 kallitype prints. The use of distilled water or water with a neutral or slightly base ph is important. Acidic water accelerates the tendency of thiosulfate to bleach highlights formed by the silver nitrate in your print.

#### <u>Paper</u>

Many papers can be used to produce a Kallitype. The final print quality depends on a number of factors but the choice of paper and your ability to coat it uniformly with the sensitizer will significantly affect your results. Please be advised that coating paper well takes a little practice so to conserve chemicals and paper the photographer might start with 4x5 or 5x7 images.

We have produced excellent results with:

Arches Watercolor 140# Hot Press – factory sized with gelatin

Others have reported success with Arches 90# Hot Press, Strathmore Artist 100% rag, and Cranes letter paper.

Papers may be "sized" with arrowroot starch, gelatin, or other materials. We supply arrowroot starch in the kit for this purpose. Sizing affects the porosity of the paper and the degree to which `the image will be imbedded in the fibers of the paper but sizing isn't always necessary. Excellent results can be obtained with un-sized paper. Papers sized with arrowroot starch generally print with a brown color while those sized with gelatin (Catalog Number 10-0590) may produce a "colder" tone. If you choose to size your paper make sure to skim off the scum after cooling the boiled starch, avoid any large clumps in the mixture, and apply uniformly and not to thickly.

## **Paper Sizing**

**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 to make. In the past this limited the creation of kallitype photographs to those who owned a large format camera. The modern photographer has computer based tools which allow for the creation of negatives on very high quality transparency materials which may be used much the same as with a traditional negative. The photographer may start with an image taken with a digital camera, a scanned negative, or a scanned print.

Any photograph may be used to create a Kallitype but the best negative for this purpose contains more contrast than one used to create a traditional silver gelatin print. This may be accomplished by the large format photographer by selecting a subject under high contrast lighting and/or by developing the film 50% or so longer than normal.

The modern photographer has the advantage of adjusting contrast in Photoshop (Adobe Trademark) or other photographic computer software. The contrast in a low contrast image might be boosted 10, 20, or even 30 percent to allow it to print more effectively as a Kallitype. Please remember however, that your choice of image and techniques for pre-print image processing are within your creative control.

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Once you have loaded or scanned the image into your photographic software and applied any contrast, lighting, or other adjustments you must apply a "Kallitype Adjustment Curve". The

purpose of this adjustment is to compensate for the filtering effects of printer ink on the transparency which blocks and transmits ultra-violet light differently than does the silver emulsion on a conventional negative. This curve is highly dependent on the printer and printer inks. A curve used to produce a negative printed on one type of printer will likely not produce the same results on a different printer. This is unfortunate, but the computer and photo software savvy individual may be able to "tweak" the curve to produce good results. It's certainly worth a try.

Should you wish to create a kallitype but don't have the equipment or facilities to create the negative we can help. Contact the Photographers Formulary and ask us about digital negatives for your project.

# Sensitizing the Paper:

Working in a darkroom under a safelight or under very subdued incandescent lighting mix equal amounts of the ferric oxalate 20% and silver nitrate 10% solutions. This is accomplished with "pipettes", one for each solution and provided in your kit. Measure and add the amount of each solution to be combined to a small cup such as a shot glass. Mix it together by simply swirling the solution around in the bottom of the container.

The sensitizer solution is mixed in equal proportions and the amount needed depends on the size of your image and the porosity of the paper. A little extra is necessary on the first paper coating as you are beginning with a clean brush. Most research shows that the best print density will result from our recommendation of equal proportions. Some studies show that slightly better densities can be achieved with slightly more silver nitrate solution. Adjust the sensitizer proportions to produce prints that meet your expectations.

In general, you can expect to use about  $\frac{1}{2}$  ml (10 drops) of each solution for a 4x5 print. An 8x10 print will require between 1 to 2 ml (20-40 drops) of each solution. Again, this is dependent on your paper and the correct amount will be determined with practice. Your kit should produce enough sensitizer to produce about twenty five to thirty 4x5 or seven to ten 8x10 prints.

After mixing the sensitizer solutions in the small container pour the solution onto the center of the paper. Then, using a high quality soft bristled brush or a foam brush very lightly spread the solution over the print area. Remember, your paper will generally be somewhat larger than your print area to allow for a border. Brush the sensitizer from left to right / right to left and from top to bottom / bottom to top then diagonally from the corners. A very light touch is preferred to avoid raising the nap of the paper. Continue until the sensitizer is evenly spread. Hang the paper to dry in the dark.

You may wish to use a hair dryer to speed up the drying time. Avoid using the high heat setting. Once dry, carefully examine the coating to see if it shows brush strokes or thick / thin spots. You may want to spread a second coat as needed.

## **Exposure**

Ferric oxalate absorbs light in the ultra violate region of the spectrum. Therefore, you will not be able to expose your print with a photo enlarger. Use the UV light from a specially designed box, a sunlamp, or that great ball of ultra violet light in the sky – the sun. Sunshine works well but it is difficult to get consistent results due to cloud cover, the time of day, or time of year. So, we recommend the use of a sunlamp; a General Electric 275 or 300 watt UV bulb is satisfactory.

PHOTOGRAPHERS FORMULARY Glass absorbs UV light so if you are printing with a sunlamp or other relatively low power light source it is advisable to print without a glass covered printing frame. In the darkroom, tack the sensitized paper to a board, position the negative on it, and pin it down. Place the board directly beneath the sunlamp (12" to 18" away). The lamp generates considerable heat so use care not to place the lamp too close. Ferric oxalate is extremely slow. Exposure will take 10-20 minutes. It is advisable to run a test strip for exposure to calibrate your setup.

The photographer may also use a UV light box to print Kallitypes which will reduce exposure time and improve consistency. The Photographers Formulary manufactures UV light boxes or they may be obtained elsewhere. These boxes increase the intensity of the light and will therefore facilitate the use of a glass covered contact print frame (also available from the Photographers Formulary) with greatly reduced exposure times in the neighborhood of 4 to 6 minutes. Again, you should calibrate your equipment with test strips to obtain an optimal exposure.

# **Development**

This kit uses sodium citrate in a 20% solution for development. Contrast may be increased by adding small amounts of potassium dichromate to the developer solution. This substance is not provided with this kit but can be obtained as part of the Photographers Formulary traditional kallitype kit or upon request.

It is important that the developer flow across the sensitized and exposed surface smoothly and evenly to prevent streaking. There are a number of ways to accomplish this. One method is to first pour the developer solution into your tray. Tilt the tray so the developer pools at one end. Hold the paper face up in the tray without contacting the solution. Quickly lower the tilted tray back to the horizontal while allowing the developer to flow across the paper. Once you get the hang of it, this will allow a smooth and even flow of developer across the paper surface.

Develop for two to three minutes with constant agitation. The image will appear almost immediately but develop for the full two minutes to allow the developer to react with all available iron and silver in the sensitizer. Note a residual black substance forming from and next to dark tones. Actively agitate the print so this substance does not stick to the highlights. The black residual accumulates in your developer and may be filtered out through coffee filters if necessary.

## **Clearing:**

Once development is complete, residual iron compounds must be cleared from the paper. Most of these have dissolved into the developer but some remain in the paper's fibers. This is accomplished in a series of clearing baths of citric acid 3%; we recommend two but a third may be used as well.

Clearing baths are moved up in rotation to always have the freshest chemical solution as the last bath. Remove the print from the developer and allow excess liquid to drain before placing it in the clear solution.

The useful life of a clearing bath depends on a variety of factors but should easily allow for two or three 8x10 prints. You are supplied with 5 liters so the solution should be allocated to your clear baths to produce ten 8x10 prints. To extend the life of the solutions, the print can be rinsed with fresh water after development and before being place in the first clear solution. The water must have a neutral or slightly acidic ph. Water with a base ph will make the print difficult to clear. Clear the print until the whites appear free of a yellow or grey fog. If the print is taking longer than 10 minutes to clear your paper is probably too absorbent and it will be necessary to size it before applying the sensitizer.

#### **Toning**

The available literature suggests that a Kallitype should be toned to improve its archival stability. Further, to avoid bleaching the highlights it is suggested that the print be toned prior to being placed in the fix solution. Practically, the photographer may want to see how the print turns out before committing it to an expensive solution of gold, platinum, or palladium. So we suggest you skip the toning step until you see how the print turns out. You may tone the print later after it has dried and you have had an opportunity to examine it closely. Re-soak the print and place it in the toning solution per directions for that toner. If your masterpiece is suitable for multiple copies you might tone it at this point of the sequence in your next run.

# **Fixing**

The fix removes any residual silver nitrate remaining in the paper. Before fixing or toning a print, rinse it well in running water to remove the clear or toning solutions. Soak the print in a weak (5% solution) of sodium thiosulfate for two to five minutes. The fix bath tends to bleach highlights so you will likely want to compensate by over exposing the print prior to development. The plain sodium thiosulfate solution is not stable for long periods so it is advisable to use it as soon as is feasible. If you are not using the entire contents of the kit return the fix solution to its container and try to schedule the use of the remaining solution at some point in the near future. You are provided two packets of sodium thiosulfate crystals. Manage your printing to allocate the equivalent of five 8x10 prints to the first fix solution and mix a fresh fix for the remainder.

We are often asked if it is OK to use the more active rapid fixes to fix a kallitype print. The available literature does not recommend it but we suggest that a weak alkali (such as PF TF-4 or ph neutral PF TF-5) fix solution diluted from 1:9 (10%) to 1:19 (5%) is suitable if a sodium thiosulfate fix is unavailable.

## <u>Final Wash</u>

The sodium thiosulfate from the fix bath must be completely removed from the paper to ensure print stability. Wash the print for 40 minutes in running water at approximately 20C, 68F. A more effective procedure is to rinse the print in water, place it in a solution of sodium-sulfite hypo clear (cat. No 03-0165 – not supplied with kit) for a five minute soak followed by a 15-20 minute final wash.

## **Final Notes and Suggestions**

Wear gloves and eye protection when mixing chemical solutions or coating paper.

Do Not use containers or utensils for food or beverages if they have been used to mix photo chemicals.

To mix the small quantity of silver nitrate, first open the silver nitrate packet and pour the premeasured 2 grams into a small mixing container. In a separate container heat 50-100 ml distilled water to 125F. Measure 20 ml of the warm distilled water and add it to the mixing container containing the silver nitrate. (20ml = 4 teaspoons) Stir until dissolved. Carefully pour the solution into the small bottle provided.

Ferric Oxalate and Silver Nitrate are light sensitive. Your 20% ferric oxalate solution and 10% silver nitrate solution are stored in dark brown bottles to prevent the solutions from losing their photosensitive properties. Don't allow them to set for long periods with the cap off. If you don't plan to use them in one session store them in a cool dark place. Ferric oxalate is best fresh but our tests show that it will remain suitable for printing over longer periods if stored properly.

PHOTOGRAPHERS FORMULARY Try using a foam brush to spread the sensitizer on the paper. The brush will absorb some of the sensitizer solution at first so it is advisable to compensate by increasing the amount of the combined ferric oxalate and silver nitrate about 30% for the first paper coating. Using Arches Watercolor 140# paper a good single coat should be obtained with:

4x5 Image	6-8 Drops of each solution
5x7 Image	8-12 Drops of each solution
8x10 Image	12-20 Drops of Each solution

Coated papers can be viewed under weak and indirect incandescent lighting but they will fog if left exposed to too bright of light. Coated Kallitype paper should be used within an hour or two after drying so prepare just as much paper as you will need for a print session.

Some photographers report that kallitype sensitizer chemicals can be mixed and coated papers viewed under incandescent lighting from a 40w bulb if the bulb is at least 6 feet away. Use your own judgment. Our recommendation remains to keep lighting low level and if possible, indirect.

Photographers Formulary can provide Photoshop density adjustment curves for many alternative print processes, including kallitype. The naming convention of the curve follows the conventions outlined in their book "Digital Negatives" by Ron Reeder and Brad Hinkel. The curves read left to right:

Printer - ink set - transparency - process - other

2400-K3mk- IPT-KT acv

Epson 2400 – K3 chrome inks – Ink Press Transparency Film – Kallitype

One of the more interesting ideas for this process is to scan an old photograph into your computer and use the image to produce a genuine kallitype with that "old school" look and feel.

There are a variety of variations in sensitizers, developers, and clear solutions available to create a kallitype photograph. Contact the Photographers Formulary for information and supplies to meet your kallitype printing needs.