

Kallitype

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A brief introduction

Adapted from Dick Stevens' Formulas

by Dick Sullivan

The Kallitype process dates to the late 19th Century. Often considered to be the poor cousin to the platinum print, it has not received the reputation that it truly deserves today. This may be in part due to the suspicion that it is not permanent. It is true that very early Kallitypes made before fixation was understood may have quickly faded, but my own suspicions are that they may be more permanent than many have suspected. Let me digress for a moment on this important point.

The Kallitype was without a doubt a very popular process in the 1880-1920 period of time. Many articles were published on how to make them. I have read more than one complaint published during this period that scoundrels were submitting Kallitypes into juried competitions disguised as platinum prints. Platinum printing was then, as it is today, an expensive proposition. I believe that this complaint was probably justified and I don't doubt that such chicanery was occurring.

I would also note that vintage Kallitypes from this period are rare today. I've asked a number of curators, photo historians, dealers and collectors about this and they all concur on this point. Interestingly too, is that they don't see a lot of faded and discolored Kallitypes lurking about like albumens have a habit of doing.

This leads me to my supposition:

1. Many Kallitypes were made in the Classical Period c. 1880-1920.
2. They were to the eye, indistinguishable from platinotype (platinum) prints.
3. Few exist from this period today

Therefore:

I propose that most are still masquerading as platinum prints. Since the only way to determine the true pedigree of the print is to subject it to very expensive x-ray spectroscopy or chemically damaging testing. I think most dealers, curators, and collectors find it easy to just assume they are platinum prints and just let it be at that. Since platinum prints are deemed more collectable and valuable than lowly Kallitypes, there is an incentive is to label them as such.

Carlos Gasperinho of Lisbon Portugal is dedicated Kallitype printer drove his car around sunny Lisbon with a Kallitype print in the back window for a year and a half to test the archivalness of Kallitypes. He has reported that he took the print down as he felt the point had been proven. It was still unfaded..

Making the Elegant Kallitype

The Emulsion

Take equal parts solution of:

Solution "A" (10% Silver nitrate solution)

Solution "B" (oxalic acid free 20% ferric oxalate solution)

1 drop of 50% Tween 20 [™] per emulsion for an 8x10 print may be used as a spreading agent and surfactant..

Use about 24 drops of each Solutions "A" and "B" per 8 x 10. The amount may vary according to the paper used.

Contrast

Advanced printers may adjust the contrast with small additions of 2% ammonium dichromate. If one drop is too strong dilute the solution.

Coating

In a dimly lit room, coat paper with either a brush or coating rod. The paper should be liberally coated but not running wet.

Resting

After coating, allow the paper to sit for about 1 to 2 minutes. The Tween 20 [™] will help even the coating out and pull it into the paper

Drying

Dry under gentle heat. A hairdryer works fine or you may just let it air dry naturally if you are not in an extremely moist climate.

Printing

Contact print under sunlight or a UV light source. Print times are about 1 to 2 stops faster than traditional palladium and about the same speed as the Ziatype. There will be little print out image so timing will have to be done by trial and error or test strip. Kallitype prints will bleach in the fix, so either tone before fixing or overprint by a stop or two. These are the only effective solutions to the bleaching problem.

Developing

Place in the developer of your choice for at least one minute. Image will appear immediately so this must be done quickly, or else watermarks may appear. Holding the print in your hand over a tray and pouring the developer from a pitcher while dropping the print and quickly rocking the tray works well for some printers.

Fixing

Fix in dilute sodium thiosulfate of 25 grams to 1 liter of water. Water should be somewhat near the 68 degrees F. range as too warm will accelerate the bleaching. Fix for only 15 seconds and then quickly place in a tray of fresh water. This amount of fix will be sufficient for fixing 10 8 x 10 prints. It should be discarded after each printing session.

Clearing

Rinse in the fresh water for 30 seconds or so, then clear for 3 to 5 minutes in a

bath of EDTA Tetrasodium of 20 grams to 1 liter of water. The EDTA may be reused until approximately 20 8x10's have been cleared.

Final Washing

Wash for 5 minutes and dry on archival blotters or screens.

Toning

Kallitype prints may be toned with any of the noble metals. Toning is one way to keep Kallitype prints from bleaching during the fixing process, however, there will be color shifts and you will lose the prints original color. Toning will also increase the permanence of the Kallitype print.

Toning formulas

To 1 liter of water add 5 grams of citric acid.

Add to this mixture either:

5 ml of gold chloride 5%

or

5 ml of standard palladium solution No. 3

or

5 ml of standard platinum solution No. 3

After development and a thorough wash, place print in toning bath. Tone until desired color is reached. The noble metal salt in the toning bath will become depleted. A black deposit will appear in the bottom of the tray, which is silver that has been replaced by the noble metal. You may now fix, clear, and do the final wash. If a sufficient toning has been done, the print will not bleach back.

One of the joys of handcoated photography (come might call it a curse) is the fact that there are many different opinions and ways to make the various kinds of prints. Beginners will probably be better off ignoring these side issues as they may be confusing, whereas the advanced printer might find them illuminating.

Carlos Gaparinho's notes on his preferences with Kallitype printing.

- 1.) I do not like Dick Stevens' formulas. I prefer much more concentrated solutions of ferric oxalate and silver nitrate. Images are a lot easier to control and much more fade resistant. I use ferric oxalate solutions up to 50% concentration.
- 2.) Ammonia is a very important part of the fixing bath. I fix for about 3 minutes and the fading is very slight. No more than one stop, which is easily compensated by the drying down process.
- 3.) The only historical formula that somewhat resembles mine was published by Nelson C. Hawks in "The Camera Craft" of 1916 and republished in the "Photo Miniature" of January 1922. If you remove the potassium oxalate as a saturated solution you will end up with Fe. Ox. at 47% and silver nit. at 17%.
- 4.) I tone most of the Kallitypes that I sell. Pt, Au or both. Final color is determined by the toner and by the initial color of the Kallitype, which depends not only from the developer used but also the sensitizer. Using the same sodium acetate developer and changing the relative quantities of Fe. Ox and Silver Nit. I can get from sepia to deep black.
- 5.) I use only one drop of dichromate (potassium works better) per 4x5 print. I change the dilution of the dichromate to change the contrast.
- 6.) The drying process is VERY important. The print must be surface dry and then quickly dried back and front with a very hot hair dryer.
- 7.) Print in my car hasn't changed in about 1 1/2 years. I finally removed it. Point proven.

Variations in the Kallitype Process

Some brief notes by Peter Marshall (petermarshall@cix.compulink.co.uk)

In the early 1840's Sir John Herschel was the first to exploit the light-sensitivity of iron(III) salts in the production of photographic prints from negatives. In the presence of light, iron(III) is readily reduced by suitable reducing agents to give iron(II). Herschel demonstrated a number of methods by which this iron(II) could then react further to produce a visible image by reducing metallic salts. He demonstrated that silver salts gave an image of silver (an Argentotype or Kallitype print), similarly platinum or palladium salts gave platinum prints, and gold gave gold prints or Chrysotypes. The iron(II) could also be used to produce a brown copper(I) oxide image by reducing copper(II) compounds. Herschel also introduced the Blueprint or Cyanotype, where the iron(II) in combination with hexacyanoferrate(III) ions forms the highly coloured complex Prussian Blue.

The iron salt used was normally combined with a suitable reducing organic anion - such as oxalate, tartrate or citrate necessary for its reduction in the presence of light. Often these anions were used as their iron ammonium salts, which can normally be readily crystallised. For many purposes it is not actually necessary to isolate the pure iron compounds and they can often be prepared more cheaply and conveniently as solutions. Although iron(III) oxalate, for example, is readily available it can be made (see Appendix) cheaply and easily as the 20% solution normally required in Kallitype or platinum chemistry. Two methods are given here, one is much simpler but has the possible disadvantage of producing a solution which also contains nitrate ions. Recent work by Mike Ware on an improved Kallitype process (the Argyrotype process) identifies the presence of oxidising anions - such as nitrate - as a major weakness of traditional methods. Such ions tend to oxidise the silver image, thus reversing the process by which it was formed and dissolving it as silver(I) ions. I have however used the solution prepared by this simple method with success for both Kallitype and platinum prints..

[Incidentally, according to the literature, blue prints may be made using the cheaply available iron(III) chloride and potassium oxalate/oxalic acid mixtures in place of the more expensive iron salts normally specified. Still having a large bottle of the green iron ammonium citrate I have yet to investigate this personally.]

Many earlier investigators applied themselves to the improvement of the iron/silver (Kallitype) process and countless variations exist. These were often minor and sometimes accidental - several much copied accounts include incorrect transcriptions of earlier work and mistakes in converting weights and measures occur frequently. One major reason behind these experiments was a desire to improve the image quality, in particular to match the properties of the much more expensive platinum process. James Thomson in the early years of this century claimed to have produced results which very closely resemble platinum prints, and it was this that led me to repeat his methods. His use of sensitisers with little or no silver also offered considerable economies. - the silver containing developer could be reused and only small amounts of silver were wasted in processing. I have made a number of prints following (with minor variations) his methods achieving good results on various papers. As Mike Ware⁶ suggests, the use of a surfactant such as Tween 20 could control the absorption of solutions for best results on some surfaces. Possibly the gum

Arabic in older formulae - such as Thomson's - performed a similar role. Increasingly as I worked with his process I began to suspect that in the earlier years of the century Thomson had arrived at solutions to many of the problems that those working with the process in its current revival are still attempting to solve. Another advantage of the older methods is that they seem generally less sensitive to variations in the paper used.

A further spur to experimentation with the Kallitype was its notorious susceptibility to fading. As Mike Ware⁶ has again clarified, the permanence of Kallitype prints depends largely on the removal of all residual iron compounds. Alkaline developers- such as the buffered borax/tartrate mixtures in common use - are likely to produce insoluble iron(III) hydroxide that is impossible to remove. Dallas Simpson gives details of a complex and ingeniously buffered silver developer to reduce this possibility. Using potassium sodium tartrate (Rochelle salts) without borax as developer would also be expected to improve permanence. Thomson's method - outlined below - uses a simple mildly acidic developer and this was yet another reason for my attraction to it. Depending on the nature of the sensitiser and also on the moisture content of the paper, the Kallitype process may be largely a printing-out process thus eliminating the need for a developer (or using water as 'developer') and prints produced by such variations (eg the Van-Dyke process) are also more likely to be permanent.

Similarly it is probably best to avoid the alkaline thiosulphate solution often recommended as a fixer - neutral (and very dilute) sodium thiosulphate does the job well. Acidic fixers should also be avoided, as bleaching of the image may occur under acidic conditions. Following fixing and washing, dilute citric acid may help to remove yet more of the residual iron salts. Gold-toning of the silver image - using conventional gold toners - should also give some protection to the image. Platinum toning was also used in the past and presents no problems other than the cost of the toner. Selenium might also be worth experimenting with, although some preliminary tests I did were not encouraging..

The majority of the superb vintage platinum prints from the golden age of platinum were on mechanically coated paper which was available in many variations and surfaces from 1879 to 1941. Commercial production of platinum/palladium paper was restarted in 1988 and the currently available (for example from Silverprint) Palladio paper is a very fine example of such a material.. Unless you find the fairly smooth paper on which it is coated too bland, there is now little incentive to coat one's own paper.. In contrast, Kallitype was always a process for experimentation (Nicol himself briefly attempted to market a commercially produced paper but this was rapidly withdrawn because of its impermanence.). Any Kallitypes still visible are virtually certain to have been made on hand coated paper, often by workers who had their own individual ideas for combating the problems inherent to the process. To print Kallitypes you have always had to make your own paper and processing solutions; that some vintage prints are still in good condition with no signs of fading proves that it was possible to use the traditional processes with success.

APPENDIX

All normal safety precautions for handling chemicals should be observed in attempting the preparation and use of any of the following. In particular, attention is drawn to the poisonous nature of all soluble oxalates. Materials data sheets can be obtained from the suppliers of all chemicals which give details of the hazards involved.

FERRIC OXALATE (IRON(III) OXALATE) SOLUTION : SIMPLE METHOD

I suggested and used this 20% ferric oxalate solution when assisting Terry King with workshops some years ago. We used it successfully in place of ferric oxalate in a number of formulae. Like most ferric oxalate solutions in old formulations it contains a small amount of oxalic acid.

iron(III) nitrate nonahydrate 8.5g
potassium oxalate monohydrate 5.8g
oxalic acid 0.25g

In subdued light, dissolve in distilled water to give 20 ml, store at least 24 hours before use. Keep in brown bottle.

This solution contains nitrate ions which may cause some solution of silver images to dissolve in some processes.

FERRIC OXALATE (IRON(III) OXALATE) SOLUTION

This is a well known method, published (with slight variations) in various sources.

Carry out in subdued or safe light.

Dissolve 42 g ferrous ammonium sulphate $[(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}]$ in the minimum quantity of distilled water. (You can also use the cheaper ferrous sulphate, $[\text{FeSO}_4 \cdot 7\text{H}_2\text{O}]$, in which case 30 g are required, and the water should be acidified with a little dilute sulphuric acid before dissolving the compound.)

Dissolve 13.0 g oxalic acid in about 100ml water and add to the ferrous sulphate solution. Allow the precipitate to settle, decant off the clear solution and discard. Add distilled water stir, allow to settle and again decant. Repeat 3 further times.

Add a further 7.5g of oxalic acid in about 70 ml of water to the solid.

Add 30% hydrogen peroxide solution in small portions with stirring until clear green solution is obtained there is no effervescence on addition. (The amount required is very variable as the peroxide solution deteriorates on keeping.) Test for the presence of ferrous compound (see below) and continue addition as necessary until a negative test is obtained.

Make to 100 ml for use.

TEST FOR FERRIC OXALATE SOLUTION

To 5 drops of the ferric oxalate solution add 1 drop potassium ferricyanide. Anything more than a slight blue colour shows the presence of significant amounts of ferrous compound, and more peroxide should be added.

SOURCE OF ALTERNATIVE PROCESS GRADE FERRIC OXALATE

Ferric oxalate can be obtained from specialist suppliers of materials for alternative processes, in particular:

BOSTICK AND SULLIVAN
PO Box 16639
Santa Fe, NM 87506-6639
505-474-0890
Hours: 9:30 am-5pm

Dick Sullivan can be contacted by email as richsul@roadrunner.com
They will send catalogues on request and ship items to the UK. As a guide, 100 gm bottle of ferric oxalate powder is currently \$47.00.

Ferric oxalate from non-photographic suppliers may contain too much iron(II) to be suitable for photographic purposes.

SILVER DEVELOPMENT KALLITYPE PROCESS

This is taken - with minor changes - from the article by James Thomson in The Photo-Miniature, Vol. VI Dec 1904, No. 69 ; amounts have been converted into metric units. The instructions have been rewritten for clarity. Like all such formulae, it should be regarded as a starting point for experimentation rather than a stone tablet. The copper(II) chloride was probably intended to remove any iron(II) present as an impurity in the ferric oxalate and may probably be omitted without loss of quality, although, as mentioned above it may also form some copper(I) oxide as a part of the image..

[This sensitiser may also be used to produce platinum prints by using a platinum containing developer in the place of the silver developer given here.]

Kallitypes produced by this process can be difficult or impossible to distinguish visually from platinum or platinum/palladium prints, although they may lack the long-term permanence of these.

To a brown bottle, add in order given without shaking:

water 14 ml

ferric ammonium citrate 1.67 g (I used the green salt, although Thomson probably used the brown.)

ferric oxalate 1.0 g *

copper(II) chloride 0.54 g

potassium oxalate 2.21 g

gum Arabic 0.67 g

(* or use only 9 ml of water and 5 ml of the 20% ferric oxalate solution prepared as above.)

Then add a solution of silver nitrate (1.0g) in 15 ml distilled water, followed by 1.0 g of oxalic acid. Leave in darkness for 24 hours. Stir well and then filter through cotton or glass wool to remove only any gritty particles (the yellow heavy sediment is necessary to the process.)

Coat the paper with the suspension using a brush, wetting the sheet as quickly as possible without leaving any pools. Allow to surface dry, then use low heat (30-40°C) to complete drying. For smooth hard surfaces you may need to apply a second coat . (Adding Tween 20 might be worth investigating in these cases.)

Expose until only the deepest shadows are visible and immerse face down in the developer, turning over immediately to see that there are no air bubbles.

DEVELOPER STOCK SOLUTION

Water 100 ml

silver nitrate 9.25 g

citric acid 2.32 g

di-sodium orthophosphate 0.46 g

(Na₂HPO₄ - 12H₂O may be listed simply as sodium phosphate or as dibasic

sodium phosphate. The equivalent potassium compound may also be used - half the mass will be needed.)

For working solution, add 13ml of this solution and about 0.2 g of oxalic acid (for blue-black tones, increasing this goes towards brown-black) to 100ml water. The stock and working solution should be stored in brown bottles. Both keep reasonably well. The developer given for Satista below is probably a suitable alternative if di-sodium orthophosphate is not available.

Development should be complete in about a minute but may be continued longer if needed.

Rinse for a minute or two in clean water (avoid alkaline water - tap water may need to be made neutral or slightly acid by the addition of a very small pinch of citric acid.) and then fix in very weak plain hypo (3 to 4 g in a litre). Wash and dry.

In view of Mike Ware's comments on causes of fading in the Kallitype it might be wise to investigate the use of a further hypo clear or citric acid bath or baths after fixing and a short wash to remove any residual iron salts from the paper.

SATISTA PROCESS

In 1913 the Platinotype Company patented the Satista process, an attempt to produce prints resembling platinum but containing a much smaller amount of platinum together with the less expensive silver. Marketed the following year, this does not seem to have been particularly successful commercially, but was apparently still available until the early thirties.. Thomson also published the formula below for those wishing to make similar prints - it differs from the patented formula in using a silver developer. Figure 1 - despite the inadequacies in reproduction - suggests the delicacies in tone available in prints made by this process. The original is a cold black and virtually identical to a pure platinum print made from the same negative, although the separation of mid-tones is possibly slightly better. There is no fading visible in this print after over four years (unfortunately this cannot be said for some of the Kallitypes I made using the borax/Rochelle salt developer.)

PLATINUM SOLUTION

Potassium chloroplatinite 1.0 g
20% ortho-phosphoric acid 6.5 ml
water to 65 ml

[To avoid any chance of expensive mistakes, the formula of the platinum compound is K_2PtCl_4 and it is the salt used in traditional platinum printing.]

Given the high cost of platinum compounds you may wish to prepare the diluted acid solution without platinum and only add the platinum compound as required for use.

SENSITISER

This sensitiser may also be used for platinum prints - a platinum containing developer is then required rather than the silver developer given below. It enables platinum prints to be produced using approximately one half to two thirds the normal amount of platinum per print

It may also - without the platinum solution - be used for Kallitypes.

Ferric oxalate solution (20%) 5 ml
water 20 ml
ferric ammonium citrate (green) 1.0g
potassium oxalate 1.0g
platinum solution (see above) 0.5 ml
potassium dichromate solution (5%) 0.05 to 0.5 ml (alters contrast)
gum Arabic 0.5 g
Stand for 24 hours before use.

STOCK DEVELOPER SOLUTION

Water 48 ml
silver nitrate 4.0 g
citric acid 1.0 g
oxalic acid 1.0 g

Use 1 + 7

Processing is exactly as for the Kallitype above, although the developer formulation given differs slightly - probably either could be used for either process.

I have also experimented with various other developers containing silver for both the Kallitype and Satista sensitisers above, including silver ammonium carbonate and other similar solutions. However, being alkaline, their use is probably not to be recommended. The buffered ammoniacal silver tartrate proposed by Dallas Simpson⁷ would appear to be a more suitable choice for rod development. A syringe (without needle) is used to deposit a small amount of developer along one side of the print, outside of the picture area. A lightly held glass or acrylic rod is then used to draw this across the print - a similar technique to the coating of prints using a rod. A suitable rod can be made from a piece of glass tubing or rod roughly 10 cm longer than the width of the print, bending it at 90 degrees about 4 cm from each end. The volume of solution used has to be great enough to avoid any noticeable weakening of print values due to developer exhaustion as it crosses the print. The syringe can be used to remove excess solution from the print for re-use with replenishment if greater economy is desired.

I have also produced gold prints by similar methods, but was unable to get really satisfactory or reproducible results - the prints tended to a rather pale lilac.

Although I have carefully checked the details, some errors may have crept in (my own laboratory notes are sometimes very difficult to read for a start!). If you find any errors or have any comments or suggestions or corrections I would like to know and would hope that these could also be published here. I hope that the information here encourages others to experiment with the Kallitype and helps them to produce the results they want. Sometimes in all the concentration on details and procedures we can forget that this is what really matters.

Cyanotype Toning of Kallitypes

From Judy Seigal

As for Carlos's mention of blue kallitypes -- they're easy enough to get (as are blue VDB's) by blue toning, using your regular cyanotype formula. Take 10cc solution A, 10 CC solution B, about 70 cc of 28% acetic acid and 20 or so ounces of water. (I did that from memory so check formula before consigning your best prints to the waves.)

Making Oxalic Acid Free Ferric Oxalate

You will need:

Solution "A": 2.5 grams of silver nitrate to 25 ml distilled water.

Solution "B": 10 grams of ferric nitrate to 25 ml water.

1.) With 100 ml of ferric oxalate solution in a small beaker or cup make your initial test by taking 10 drops of the ferric oxalate solution and placing it in a small shot glass or plastic taco sauce container.

2.) Add a drop or two of the silver nitrate. If a yellow precipitate forms in 15 seconds, there is free oxalic acid. The yellow precipitate is silver oxalate.

3.) If you get the yellow precipitate, then add a few drops of the ferric nitrate and stir for about 30 seconds.

4.) Repeat steps 2 and 3 until no precipitate is formed.



Yosemite, CA

Kallitype Print, 8.5x11in, Print made in early 70's. I believe I did not clear it properly. I was new to the process and was operating on sketchy information in an old encyclopedia of photography.

There appears to be some staining in the upper left corner, but there is no fading in the image, which is supposed to be the problem with Kallitypes.

Dick Sullivan Last modified: January 11, 2003