

Siderotype Workshop Notes

Print-out Palladiotype

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Overview of Palladiotype and Platinotype

Platinotype was invented by William Willis of Bromley, UK, in 1873 and by 1892 it had become the pre-eminent printing process for artistic photography. In 1916, World War I imposed a ban on its use, so Willis offered Palladiotype as an alternative, but platinum made a come-back in 1920, until Willis's Platinotype Company was finally dissolved in 1937. For the next 40 years both processes fell into disuse, until revived in the alternative photography renaissance of the 1970-80s. Some details of this history may be found here:

http://www.mikeware.co.uk/mikeware/Eighth_Metal.html

In recent years platinum-palladium printing has regained its place at the summit of alternative photographic practice, renowned for the subtly nuanced tonal qualities of its images, formed by totally permanent 'noble' metals in matte-surfaced artists' paper. Willis's traditional platinotype and palladiotype are development processes, and capable of beautiful results – in skilled hands – but suffer from some chemical inconsistency. The method described here, known as the Malde-Ware Palladiotype, employs a better-behaved iron sensitizer, derived from the 'print-out' platinum process due to Pizzighelli in 1887. A technical comparison with the earlier process is made here:

<http://www.platinummetalsreview.com/dynamic/article/view/49-4-190-195>

This modernized version has some advantages in economy, accessible chemistry, and exposure control. Using the procedures described in these notes, a choice of the image hue anywhere between neutral grey-black and rich sepia can be achieved. A controlled degree of humidity is allowed in the sensitized paper, to promote the formation of a 'print-out' palladium image during the exposure, requiring little or no development. A carefully-devised clearing sequence ensures that all the residual iron is removed from the paper. For further details see:

<http://www.mikeware.co.uk/mikeware/Platino-Palladiotype.html>

Disclaimer

It is the responsibility of the users of chemicals to inform themselves about the risks, and to take appropriate precautions in their handling. Reference should be made to the Materials Safety Data Sheets (MSDS), which are accessible online:

<http://www.ilpi.com/msds/index.html>

The author hereby denies liability for any consequent sickness, injury, damage or loss resulting from the use of the chemicals named herein.

Chemicals for Palladiotype Sensitizer

Purity: General Purpose Reagent (GPR) grade *ca.* 98%

These quantities will make at least 30 10x8 in. Palladium prints

Substance & Formula	Quantity
Ammonium iron(III) oxalate $(\text{NH}_4)_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ <i>aka ferric ammonium oxalate; ammonium ferrioxalate</i>	30 g
EITHER	
Ammonium tetrachloropalladate(II) $(\text{NH}_4)_2[\text{PdCl}_4]$ <i>aka ammonium chloropalladite</i>	5 g
OR	
Palladium(II) chloride PdCl_2 <i>aka palladium dichloride</i> plus	3 g
Ammonium chloride NH_4Cl	1.8 g
Water, purified, H₂O (distilled, de-ionised, pharmaceutical, etc)	100 cc
Tween 20™ $\text{C}_{58}\text{H}_{114}\text{O}_{26}$ <i>aka polyoxyethylenesorbitanmonolaurate; polysorbate</i> Separate solution diluted to 10% or 5% v/v	0.25 cc

Chemicals for Processing Palladiotypes

Purity: General Purpose Reagent (GPR) grade ca. 98%

These quantities suffice to process ca. 60 10x8 in. Pt/Pd prints

Processing Solutions	Quantity
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Ethylenediaminetetraacetic acid, disodium salt $(\text{NaO}_2\text{CCH}_2)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2 \cdot 2\text{H}_2\text{O}$ <i>aka</i> 1,2-Diaminoethanetetraethanoic acid, disodium salt; Disodium EDTA; disodium edetate; Dissolve 100 g of the solid in 2 litres of water	5% w/v 2 litres
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Ethylenediaminetetraacetic acid tetrasodium salt $(\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{Na})_2)_2 \cdot 2\text{H}_2\text{O}$ <i>aka</i> 1,2-Diaminoethanetetraethanoic acid, tetrasodium salt; Tetrasodium EDTA; tetrasodium edetate Dissolve 100 g of the solid in 2 litres of water	5% w/v 2 litres
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Sodium metabisulphite $\text{Na}_2\text{S}_2\text{O}_5$ <i>aka</i> sodium pyrosulphite; sodium disulphite Dissolve 25 g (a level tablespoonful) of the solid in 1 litre of water Alternatively, sodium sulphite or sodium hydrogen sulphite (sodium bisulphite) or Kodak 'Hypoclear' powder may be used. This solution should be made up fresh for a day's printing, and not stored and re-used.	2.5% w/v ~10 1 litre batches
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Meaning of Solution Strength abbreviation:

X% w/v "weight per volume": X grams of solute in 100 cc of solution

Apparatus for Making Palladiotype Sensitizer

Pyrex glass beakers 2 x 100 cc

Measuring cylinder 50 or 100 cc

Scales or chemical balance sensitive to 0.1 g

Glass stirring rod

Conical filter funnel *ca.* 5–6 cm diameter

Filter paper Whatman Grade #1 *ca.* 8–10 cm diameter

Brown glass bottles 3 x 100 cc

Hotplate (or bath of very hot water)

Tungsten lighting to work under, not fluorescent or daylight.

Equipment and Materials for Coating and Printing Palladiotypes

Paper

Glass coating rod

Blotting strips

Syringes, at least 3, calibrated 1 cc, 2 cc and 5 cc

Mixing vessel – small liqueur or ‘shot’ glass

Glass plate

Spirit level

Drafting tape or clips

Print frame

Hygrometer

Cat litter trays – for humidifiers – with lids

UVA light source

Timer

Plastic measuring jug 2 litre

Stirrer

Processing dishes (5)

Tongs or plastic gloves

Drying line and pegs or drying screen

Preparation of Palladiotype Sensitizer Solutions

N.B. The following sequence of instructions should be carried out under dim tungsten lighting, not fluorescent or daylight

Iron solution 60% w/v ammonium iron(III) oxalate
(Volume 50 cc)

- 1 Weigh out 30 g of ammonium iron(III) oxalate into a small (100 cc) Pyrex glass beaker.
- 2 Add exactly 33 cc of pure water (from a measuring cylinder) and stir well to dissolve the solid.
- 3 The solution becomes cold, so gently warm the beaker in a bath of hot water (ca. 50°C) to assist dissolution.
- 4 The solid will dissolve to form an emerald-green solution within 5 minutes. The volume should be correct (check it's 50 cc) so it should not need to be made up.

(Any tiny residue of remaining solid may be ignored.)

- 5 Filter the solution (Whatman #1 filter paper) directly into the clean, dry, brown storage bottle, and label appropriately. Store at room temperature in the dark: the shelf life will be several years.

(If, after a few days, a few white needle-like crystals (probably of ammonium oxalate) have appeared, re-filter the solution to remove them. This solution is close to saturation; if cooled below 20°C for a length of time, green crystals may appear: warm gently and swirl to redissolve these.)

Palladium solution 19% w/v ammonium tetrachloropalladate(II)

(Two options - depending on price and availability of chemicals)

EITHER

Method 1 (Volume 26 cc)

- 1 Weigh out 5 g of ammonium tetrachloropalladate(II) and transfer into a small (50 cc) measuring cylinder.
- 2 Add ca. 15 cc of pure water to dissolve the solid by stirring at room temperature.
- 3 Make up the solution with pure water to a volume of exactly 26 cc in the measuring cylinder.
- 4 Filter the solution using a small conical funnel and Whatman Grade #1 filter paper, directly into a brown storage bottle, stopper and label it.

OR

Method 2 (Volume 25 cc)

- 1 Weigh out accurately 1.8 g of ammonium chloride into a 100 cc Pyrex glass beaker
- 2 Add 20 cc of pure water and all the solid should dissolve easily.
- 3 Heat the solution (*ca.* 70°C) and add 3 g of well-powdered palladium(II) chloride, a little at a time, with stirring.
(Hazard! Wear a dust mask).
Keep hot and stir until all the brown solid has dissolved to give a very dark red solution (which may take up to an hour).
(Carefully view the solution from below to ensure no solid remains.)
- 4 Allow to cool and transfer the solution to a small measuring cylinder, and make up to a volume of exactly 25 cc with pure water.
(Use some of this water to wash out any solution left in the beaker.)
- 5 Filter the solution using a small conical funnel and Whatman Grade #1 filter paper, directly into a brown storage bottle; stopper and label it.
(This solution is stable indefinitely.)

Making up the Processing Solutions

1. Disodium EDTA (~5% w/v)

Dissolve *ca.* 50 g of disodium EDTA in *ca.* 1 litre (1000 cc) of tap water in a large plastic measuring jug with stirring at room temperature. Capacity ~50–60 prints 10"x8" per litre.

Alternative formulation

If disodium EDTA is unavailable, and only tetrasodium EDTA on hand, the latter may be effectively converted to the former by the addition of citric acid, (C₆H₈O₇) to the extent of 31 g of citric acid to each 100 g of tetrasodium EDTA. The presence of the citrate ion can only assist the clearing.

2. Sodium disulphite (~2.5% w/v)

Dissolve *ca.* 25 g (one rounded tablespoonful) of sodium disulphite, (aka sodium metabisulphite, Na₂S₂O₅) in *ca.* 1000 cc of tap water. Use this solution for one printing session only and discard it. Do not store.

3. Tetrasodium EDTA (~5% w/v)

Dissolve *ca.* 50 g of tetrasodium EDTA in *ca.* 1000 cc of tap water with stirring at room temperature. Capacity ~100 prints 10"x8" per litre.

Alternative formulations using EDTA

If the only available chemical is the free tetrabasic acid H₄EDTA itself, and not its sodium salts, to make 5% solutions for baths **1** and **3** it may be partially neutralised by any convenient sodium alkali in the following proportions:

Dissolve **one** of the following amounts of alkali per 1000 cc of water, and add ~35 g of H₄EDTA in small portions with stirring, allowing (for the carbonates) the effervescence of CO₂ to subside:

Alkali		to make: Na ₂ EDTA	Na ₄ EDTA
Sodium hydroxide	NaOH	9.6	19.2 grams
Sodium carbonate	Na ₂ CO ₃ (anhyd.)	12.7	25.4
Sodium carbonate	Na ₂ CO ₃ .10H ₂ O	34.3	68.6
Sodium bicarbonate	NaHCO ₃	20.2	40.3

Notes on the Palladiotype Process

Choice of Paper

Avoid papers that are alkaline-buffered with chalk (calcium carbonate). The best results will be obtained on unbuffered papers such as:

- 'Buxton' or 'Herschel' handmade by Ruscombe Mill
- Arches Platine
- Weston Diploma Parchment
- Crane's Platinotype, also called Crane's Business Card Stock
- Awagami Masa
- Wyndstone Vellum
- Atlantis Silversafe Photostore

If buffered papers are unavoidable, such as Canson Lavis Technique, Fabriano 5, or Whatman Watercolour, they should be pre-treated in a bath of dilute (5% v/v) hydrochloric acid or sulphamic acid to destroy the chalk, then washed.

For prints up to 10x8 in. or A4 in size, a paper weight of 160 gsm (grams per square meter, g/m²) is adequate. For larger prints of A3 size, a heavier weight of 240 gsm, or more, will minimise cockling and "bellying" of the coated sheet due to the stresses set up by the hydroexpansion of the cellulose fibres in the wetted area. The sheet will contact the negative better, and be more robust in wet handling.

Regulation of Image Colour

Drier conditions (RH ~ 55%) yield Van Dyke brown or sepia tones and a softer image, *i.e.* a longer exposure range, with great delicacy in the high values. The tones are warmer on gelatin-sized papers than on Aquapel-sized. When well-humidified (RH ~ 70-80%), near-neutral tones can be achieved, provided that exposures are not too short in duration, and no surfactants are used.

Choice of Print Contrast

Having prepared a negative of approximately the right density range, ca. 2.4, the contrast may be fine-tuned in the printing process by regulating the humidity of the sensitized paper before exposure. The print-out process does not show a critical dependence on negative contrast because high values can be 'printed down' by prolonging the exposure without the shadows 'blocking up'.

Mixing the Sensitizer Solutions

Mix equal volumes of the iron and palladium solutions at room temperature under dim tungsten lighting. The paper may be coated immediately.

These small volumes are conveniently measured and delivered by means of disposable calibrated plastic syringes (*without* hypodermic needles!) of capacity 1, 2 or 5 cc. Dedicate a separate syringe for each

solution to avoid cross-contamination of the stock solutions, and use a third syringe for delivering the mixed sensitizer onto the paper. A small liqueur glass makes an ideal mixing vessel – provided you give up drinking out of it! Mix the solutions well by drawing the liquid gently in and out of the delivery syringe three times.

Addition of Surfactant to Sensitizer

Absorbent papers should not require any additional surfactant (wetting agent), but some hard-sized papers, such as Buxton, may yield a better, more uniform coating if a little surfactant is used.

Tween 20™ (a non-ionic surfactant) may be added to the sensitizer solution before coating to produce a final concentration of *ca.* 0.25%. Add one drop (0.05 cc) of a 5% stock solution of Tween 20™ for each cc of sensitizer and mix well (or one drop of 10% per 2 cc).

Do not add Tween to the stock sensitizer solution: it doesn't last very well, and the appropriate amount will depend upon the paper. Tween may interact unfavourably with gelatin-sized papers.

Tween also tends to promote a warmer colour in palladiotypes.

Coating Paper with Sensitizer using a Glass Rod

Paper stored at low relative humidity (less than 50% RH) may imbibe excessive amounts of sensitizer and coat unevenly. Before coating, it may be advantageous to pre-humidify the sheet to 70–80% RH (see **Humidifying** section, below). All manipulation of the sensitized paper can be carried out under dim tungsten lighting: avoid fluorescent light or daylight. Room temperature should be normal (18–22 °C), if too low the sensitizer may crystallize.

Coating by the rod method will require *ca.* 1.5 cc of sensitizer to coat an area appropriate for a 10x8 in. print. Brush coating consumes more and is expensively wasteful.

- (1) If necessary, cut or tear your sheet of paper to a size that allows generous margins around the picture area, for ease of future handling, but still fits the printing frame.
- (2) Mark the sheet of paper lightly in graphite pencil at the corners of the area to be coated – a template helps. The coating dimensions should be ~1 cm larger than the negative to allow for irregularities.
- (3) Tape or clip the sheet lightly, at top and bottom, to a very flat level surface: a heavy glass plate is ideal. Use a low-tack tape such as Scotch Removeable 3M811.
- (4) Check with a spirit level that the paper is horizontal left to right; this is critical, so adjust it if necessary by inserting spacers below the glass plate.
- (5) Dust off the surface with a blower brush.

- (6) Draw up the mixed sensitizer into a syringe of appropriate size, and adjust it to the required volume, reading from the bottom of the plunger. A trial volume may be calculated from the average specific coating volume of 25 cubic centimeters per square meter of paper surface area (25 cc/m²).
- (7) Point the nozzle of the syringe at the bottom left mark, and expel the liquid slowly and gently (use two hands) in an unbroken strip of sensitizer as you move it steadily from left to right across the width of the coating area. For steadiness, touch the paper lightly with the syringe nozzle. Do not be too slow or fussy – irregularities will even out in the coating.
- (8) Hold the spreading rod with one end in each hand, and place the straight central portion onto the paper parallel to, and a little below, the strip of sensitizer. Then, with moderate pressure, push the spreading rod up into the strip of solution. Pause briefly (2 seconds) while the liquid distributes itself uniformly along the length of the rod, then steadily push the strip of solution up the paper, like a tiny tidal wave running in front of the rod.
- (9) When you reach the pencil marks at the top of the coated area, 'hop' the rod over the strip of solution and pull it back to the bottom of the coating; then hop over the sensitizer strip once more and push it up to repeat the spreading. Just four passes over the paper should suffice for its surface layer to become saturated with a uniform coating of sensitizer. The first pass should be made quite rapidly (3 or 4 seconds) applying moderate pressure to ensure complete wetting of the surface. The last three passes as slowly as possible (10 to 15 seconds each) with very little pressure applied, to allow maximum absorption. At the end of the fourth pass, drag the spreader below the picture area with any excess sensitizer. But if much excess solution remains you can apply two more passes.
- (10) Gently lift off the spreader rod, and soak up any residual liquid left at the bottom of the coating with the edge of a clean strip of blotting paper.
- (11) In future coatings, try to “fine tune” your exact coating volume on the basis of experience with your chosen paper, in order to minimise waste.

For illustrated instructions see:

<http://www.mikeware.co.uk/mikeware/preparations.html>

Drying & Storage

It is simplest to let the sensitized paper dry at room temperature and RH, in the dark, for about an hour. Shorter times are possible, but very humid paper may damage precious silver-gelatin negatives, and not lie flat due to fibre swelling. Alternatively, allow a few minutes for the sensitizer to soak in, until the paper surface appears non-reflective, then heat-dry it with an air stream at about 40°C for *ca.* 10 minutes.

The sensitized paper should be used within a few hours; otherwise, it must be stored in a light-tight, air-tight container, in the presence of a desiccant such as silica gel or anhydrous calcium chloride, below 10% RH, in order to prevent chemical fogging. Paper may be stored for six months in this way without loss of quality.

Humidifying

The key to the print-out process of palladiotype lies in controlling the humidity of the sensitized paper just before exposure. Optimum results are obtained between 50% and 80% ambient RH. Below 50% RH there is only partial printout and considerable development, above 80% RH the maximum density of the image may tend to weaken because the sensitizer diffuses too deeply into the paper. If you have a hygrometer, you can simply make use of the prevailing relative humidity (if suitable) to achieve a predictable result by hanging the paper in a dark place at room temperature (*ca.* 20°C) for an hour or two before exposure.

If greater control is desired, a humidifying tank should be made: *i.e.* a tray with close-fitting lid, in which the paper may be placed face down, over, but not in contact with, a saturated aqueous solution which provides an atmosphere of constant, known relative humidity. Cat litter trays are ideal for this purpose; photographic dishes are too shallow and have a lip which makes sealing difficult. The sheet of sensitized paper is held securely on the underside of the lid, by two strips of self-adhesive magnetic tape, which is quick, clean, and does not mark the paper. The most useful saturated solutions are:

- ammonium chloride RH 80%
- common salt (sodium chloride) RH 76%
- calcium nitrate tetrahydrate RH 55%

It is important that there should always be excess solid salt in contact with its saturated solution, and that the paper should be evenly exposed to the vapour. The time of exposure in the humidifying tank should not be less than half an hour, to achieve evenness; the upper time limit is not critical and can be a few hours.

A simpler method of humidifying is to use pure water in the tank, which therefore contains an atmosphere of 100% RH; but in this case the timing of the humidification is critical: from 5 to 20 minutes for a warm-toned result; a longer humidification of 30 to 40 minutes in the water vapour will yield fuller print-out and a colder image tone.

Humidification at RH 100% for more than one hour may lead to weaker image density, and clearing problems. Over-humidified paper is also more likely to damage negatives during contact printing.

Printing Exposure and Negative Masking

Negatives should have a long density range (in the UV): ca. 2.4 for palladiotype, to produce a full tonal range in the print – as for my other siderotype processes. Exposure is a few minutes under an average UVA light source. With an 800 W HID UV lamp and digital negatives exposure is ca. 40 s.

Since this is substantially a print-out process, a hinged-back contact printing frame enables intermediate inspection of the result: under conditions of full print-out (80% RH) continue exposing until the highlight detail is resolved; the shadows will not ‘block up’ totally, like development papers, because the printing-out process has a self-masking action in regions of high print density.

In all the siderotype processes, including palladiotype, one of the by-products of the photochemical reaction is carbon dioxide gas. The quantity of this gas if it is ‘trapped’ may be sufficient to cause a loss of image acutance (edge-sharpness or resolution) in regions of high local contrast, depending on the nature of the light source. It is therefore important to the quality of the print that this gas should find a pathway to diffuse out from the sensitized surface, otherwise it will form a ‘bubble’ interposed between negative and paper which may be thick enough to degrade the resolution of the image, especially if a ‘light bed’, rather than a ‘point source’, is providing the illumination. The permeability of the printing paper should be sufficient to allow passage of the gas through to its *verso*, and it is important that the paper sheet should *not* be backed by an impervious plastic sheet in the printing frame, but only with a felt blanket of the kind used by papermakers, or other material permeable to gases, which will absorb the CO₂.

The author believes that it is preferable to mask the borders of the coated area rather than show the rough edges left by passes of the glass rod or by brush strokes. There are three reasons for this preference: aesthetic, technical, and practical. Aesthetically, it seems unnecessary to ‘show the brushmarks’ in order to prove that it’s a handmade print. Connoisseurs will already know that anyway. Moreover, an erratic black border forms a strong peripheral distraction from the image content. The formal, geometrical qualities of the rectangular frame have the time-honoured virtue of being unpretentious.

The technical reason is most important: the masked margin that has been coated with sensitizer, but remains unexposed, provides a direct visual test of the complete clearing of excess chemicals from the print during the wet processing, by comparison with the uncoated paper bordering it. If the margins are not masked, but exposed and

darkened, one can never tell if the print has been properly cleared. It can be a cruelly demanding test – but very desirable!

In practical terms, if there is a large non-image area of redundant sensitizer which is heavily exposed, the dense photoproduct may "bleed" during wet processing, into light image areas like sky, and ruin the print. Moreover, an unnecessary excess of CO₂ gas will be produced. Masking the print with 'Rbylith' or black polythene costs nothing except a little care and precision – the hallmarks of good craftsmanship.

Wet Processing Procedure

1 "Steam" the print (an optional step: 'post-hydration') 1–2 mins

To enhance the gradation in the high values, especially if print-out is not complete, expose the print surface uniformly to water vapour over a tray of water at *ca.* 40°C.

Then immerse it in the following wet-processing baths, face down if it floats, face up if not, with intermittent agitation:

2 Develop in disodium EDTA (5% w/v) 10 mins

It is important that this first bath should be acidic, pH ~4. Do not use tetrasodium EDTA. Its capacity is *ca.* 60 10x8 in. prints. When spent, this bath should be saved for recovery of precious metal.

3 Rinse in water half min

4 Clear in sodium metabisulphite (2.5% w/v) 10 mins

This sulphite bath does not keep, so should not be stored and re-used, but made up fresh for each printing session.

5 Rinse in water half min

6 Clear in tetrasodium EDTA (5% w/v) 10 mins

The capacity of this two litre bath is at least 60 10x8 in. prints.

7 Wash in running water for a minimum of 30–60 mins

8 Drain face out, on a near-vertical sheet of Perspex 10 mins

9 Dry at room temperature on a horizontal plastic / fibreglass screen.

Examine the print for any yellow stain of residual iron in regions of unexposed sensitizer; this is more conspicuous under a bluish light. If present, prolong Bath 6.

Finishing

The print is easy to retouch using permanent watercolour pigments.

Permanence & Stability

Palladiotypes are highly lightfast and may be displayed under good lighting. They are robustly resistant to all contaminants likely to arise in a normal environment.

Summary of Palladiotype Workflow

1. **Unbuffered paper:** pre-humidified to ca. 70% RH. Choose side, wire or felt, and mark up coating area with a template
2. **Mix sensitizer:** measure and mix equal volumes of iron and palladium solutions; add Tween to ca. 0.25% if needed
3. **Coat paper:** ~1.5 cc per 10x8 in. 4 to 6 'passes' of rod
4. **Dry:** 1-2 hours at room temperature, or hot air for 10 minutes
5. **Negative:** density range ~2.4 in the UVA
6. **Humidify coating if necessary:** 80% for full print-out
7. **Expose:** to UVA source until highlights just visible
8. **"Steam"** the print over 40°C water for 2 minutes (optional)
9. **Develop and Clear #1:** Disodium EDTA 5% for 10 minutes
10. **Rinse** in water
11. **Reduce and Clear #2:** Sodium metabisulphite 2.5% 10 minutes
12. **Rinse** in water
13. **Final Clear #3:** Tetrasodium EDTA 5% for 10 minutes
14. **Wash:** at least 30 minutes
15. **Drain, Dry** and press flat