

## **Siderotype Workshop Notes**

# **Platino-palladiotype**

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## Overview of Platinotype and Palladiotype

Platinotype was invented by William Willis of Bromley 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](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 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, platinum or palladium may be used individually, or mixed in any proportion, allowing a choice of the image hue anywhere between neutral grey–black and rich sepia. A controlled degree of humidity is imparted to the sensitized paper, which promotes the formation of a 'print-out' platinum/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.

## Platinum Allergy: Health & Safety

Contact with ammonium tetrachloroplatinate(II), and other chloro–complexes of platinum, is known to cause symptoms of asthma and dermatitis; some allergic individuals may become particularly sensitized to these biologically–active chemicals. The symptoms disappear on removing the cause: if you develop this allergy, then platinum printing is not for you – but you could still use palladium. Appropriately, ‘platinum allergy’ was first observed in 1911 as an occupational disease of photographic factory workers handling platinotype paper. Never touch the surface of platinum–sensitized paper or immerse ungloved fingers in the processing solutions. It is better not to store large amounts of dried sensitized paper. Platinum metal itself is not implicated in this – so take comfort that there is no risk in handling fully–processed platinotypes!

## Chemicals for Preparing Platino-palladiotype Sensitizer

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

**These quantities will suffice to make ca. 60 10x8 in. Pt/Pd prints**

| <b>Substance, Formula &amp; MSDS</b>  | <b>Quantity</b> |
|---|-----------------|
| <b>Ammonium iron(III) oxalate</b> $(\text{NH}_4)_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$<br><i>aka ferric ammonium oxalate; ammonium ferrioxalate</i>   | 30 g            |
| <b>Ammonium tetrachloroplatinate(II)</b> $(\text{NH}_4)_2[\text{PtCl}_4]$<br><i>aka ammonium chloroplatinite</i><br><a href="http://www.alfa.com/content/msds/english/11046.pdf">http://www.alfa.com/content/msds/english/11046.pdf</a> | 5 g             |
| EITHER  |                 |
| <b>Ammonium tetrachloropalladate(II)</b> $(\text{NH}_4)_2[\text{PdCl}_4]$<br><i>aka ammonium chloropalladite</i><br><a href="http://www.alfa.com/content/msds/english/11882.pdf">http://www.alfa.com/content/msds/english/11882.pdf</a> | 5 g             |
| OR  |                 |
| <b>Palladium(II) chloride</b> $\text{PdCl}_2$<br><i>aka palladium dichloride</i>  | 3 g             |
| <b>Ammonium chloride</b> $\text{NH}_4\text{Cl}$   | 1.8 g           |
| <b>Water, purified</b> , $\text{H}_2\text{O}$<br>(distilled, de-ionised, pharmaceutical, etc)   | 100 cc          |
| <b>Tween 20™</b> $\text{C}_{58}\text{H}_{114}\text{O}_{26}$<br><i>aka polyoxyethylenesorbitanmonolaurate; polysorbate</i><br>Separate solution diluted to 10% or 5% v/v   | 0.25 cc         |

## Chemicals for Processing Platino-palladiotypes

**Purity: General Purpose Reagent (GPR) grade ca. 98%**  
**These quantities suffice to process ca. 60 10x8 in. Pt/Pd prints**

| Processing Solutions | Quantity |
|----------------------|----------|
|----------------------|----------|

|  |          |
|--|----------|
| <b>Ethylenediaminetetraacetic acid, disodium salt</b> 5% w/v<br>$(\text{NaO}_2\text{CCH}_2)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2 \cdot 2\text{H}_2\text{O}$<br><i>aka</i> 1,2-Diaminoethanetetraethanoic acid, disodium salt;<br>Disodium EDTA; disodium edetate;<br><a href="http://www.alfa.com/content/msds/english/A15161.pdf">http://www.alfa.com/content/msds/english/A15161.pdf</a><br>dissolve 100 g of the solid in 2 litres of water | 2 litres |
|--|----------|

|  |          |
|--|----------|
| <b>Ethylenediaminetetraacetic acid tetrasodium salt</b> 5% w/v<br>$(\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{Na})_2)_2 \cdot 2\text{H}_2\text{O}$<br><i>aka</i> 1,2-Diaminoethanetetraethanoic acid, tetrasodium salt;<br>Tetrasodium EDTA; tetrasodium edetate<br>dissolve 100 g of the solid in 2 litres of water | 2 litres |
|--|----------|

|  |         |
|--|---------|
| <b>Sodium metabisulphite</b> $\text{Na}_2\text{S}_2\text{O}_5$ 2.5% w/v<br><i>aka</i> sodium pyrosulphite; sodium disulphite<br>dissolve 25 g (a level tablespoonful) of the solid in 1 litre of water<br>Alternatively, sodium sulphite or sodium hydrogen sulphite<br>(sodium bisulphite) or Kodak 'Hypoclear' powder may be used. This<br>solution should be made up fresh for a day's printing, and not stored<br>and re-used. | 1 litre |
|--|---------|

***Meaning of Solution Strength abbreviation:***

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

## **Apparatus for Preparing Platino-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 Platino-palladiotypes**

Paper

Glass coating rod

Blotting strips

Syringes, at least 4, 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 Platino-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 (50 cc) so it does 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.)*

**Platinum solution** 25% w/v ammonium tetrachloroplatinate(II)  
(Volume 20 cc)

- 1 Weigh out 5 g of ammonium tetrachloroplatinate(II) and transfer into a small (50 cc) measuring cylinder.
- 2 Add 18 cc of pure water to dissolve the solid by stirring at room temperature. The final volume should be exactly 20 cc in the measuring cylinder.
- 3 Decant the solution directly into an amber storage bottle, labelled and dated.

*(Any small amount of yellow precipitate may be ignored.)*

- 4 Allow the solution to stand for at least 24 hours before first use.

*(The solution should keep for a year or so.)*

## Preparation of Platino-palladiotype Sensitizer Solutions – continued

### **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 an amber 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 see if any 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 an amber storage bottle; stopper and label it.

*(This solution is stable indefinitely.)*



# Notes on the Platino–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’ Handmade by Ruscombe Mill
- Weston Diploma Parchment
- Crane’s Platinotype
- Wyndstone Vellum
- Atlantis Silversafe Photostore

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

Do not use gelatin–sized papers for platinum–containing prints: gelatin inhibits the chemistry of platinum metal formation. They may be used for pure palladium prints, on which gelatin has no adverse effect. Papers sized with Alkylketene dimers (AKD), such as Aquapel™, or with alum–rosin are suitable for platinotype.

For prints up to 10x8 in. or A4 in size, a paper weight of 160 gsm (grams per square meter, g/m<sup>2</sup>) 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.

## Choice of Sensitizer Composition and Image Colour

Platinum and palladium solutions may be used separately, or combined in any ratio in the sensitizer in order to fulfill your wishes for the hue and contrast of the finished print:

**Palladium** yields 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, near–neutral tones can be achieved, provided that exposures are not too short in duration.

**Platinum** yields neutral tones and tends to provide a slightly higher contrast (shorter exposure range) than palladium, and greater maximum density; but the overall speed of printing may be slower, depending on the purity of the paper, which is paramount.

**Platinum–palladium** mixtures combine their characteristics proportionally, and offer a useful compromise.

## Sensitizer Characteristics

The characteristics of some sensitizers are summarised in the Table below, showing their dependence on the Relative Humidity (RH%).

- The Relative Speed is arithmetic, referring to middle tones.
- The Exposure Range ( $\Delta\log H$ ) is from fog+0.04 to  $0.9D_{\max}$
- Development is in  $\log H$  units ( $0.3=1$  stop). 0 is total print-out.
- Note that these parameters will vary with the choice of paper.

| Sensitizer               | RH % | Relative Speed | Expos. Range | Develop-ment | Colour        |
|--------------------------|------|----------------|--------------|--------------|---------------|
| Platinum                 | 32   | 1.8            | 1.5          | 0.9          | warm black    |
|                          | 55   | 1.7            | 1.5          | 0.3          | warm black    |
|                          | 80   | 1.0            | 1.8          | 0            | neutral       |
| Palladium                | 32   | 0.5            | 2            | 0.4          | sepia         |
|                          | 55   | 1.3            | 2.2          | 0.2          | Vandyke brown |
|                          | 80   | 2.5            | 2.4          | 0            | warm black    |
| Platinum–palladium (3:1) | 32   | 1.2            | 1.6          | 0.6          | warm black    |
|                          | 55   | 1.0            | 2            | 0            | neutral       |
|                          | 80   | 1.0            | 2.2          | 0            | neutral       |

Table. Characteristics of Print-out Platinum–Palladium Sensitizers

### Choice of Print Contrast

Having prepared a negative of approximately the right density range, the contrast may be fine-tuned in the printing process by two main controls: mixing of platinum and palladium in various ratios, or by regulating the humidity of the sensitized paper before exposure. The printing exposure range ( $\Delta\log H$ ) values in the Table indicate the effects of these controls.

Mixing the platinum and palladium solutions in the ratio of about 3:1, respectively gives a sensitizer with a contrast and speed that are fairly constant over wide variations in humidity (RH 40–70%), and with a long range of well-graduated neutral tones, and a good  $D_{\max}$ .

### Mixing the Sensitizer Solutions

- **For a palladium print** mix equal volumes of the **iron** and **palladium** solutions, which may be coated immediately.
- **For a platinum print** mix equal volumes of the **iron** and **platinum** solutions; for highest  $D_{\max}$  let the mixture mature for one hour in the dark at room temperature before coating.
- **For a platinum–palladium print** you may combine the **platinum** and **palladium** solutions in any proportion: then mix them with an equal volume of **iron** solution. Preferably let the mixture mature for one hour in the dark before coating.

Mixing should be done at room temperature under tungsten lighting. 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 fourth 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. To ‘mature’ a solution before coating draw it up into a syringe to minimise evaporation, and leave in a dark place.

## Addition of Surfactant to Sensitizer

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

## Coating

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).

Coating by the rod method (5–7 ‘passes’) 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. A wide uncoated border is recommended to facilitate handling. Blot off any excess sensitizer which may crystallize and damage negatives. Try to “fine tune” your coating volume on the basis of experience, in order to avoid excess. For instructions see:

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

All manipulation of the sensitized paper can be carried out under tungsten lighting, avoid fluorescent light or daylight. Room temperature should be normal (18–22 °C), if too low the sensitizer may crystallize.

## 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 platino–palladiotype lies in controlling the humidity of the sensitized paper just before exposure. The effect of ambient RH on the extent of print-out, colour and contrast is summarised in the Table above, from which you will see that 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.

Greater control, however, is provided by a humidifying tank *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. 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 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 weakening of the 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): at least 1.8 for platinum and as much as 2.4 for palladium, 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 platinum-palladium, one of the by-products of the photochemical reaction is carbon dioxide gas. The quantity of this gas so produced can be calculated,<sup>i</sup> and if it is 'trapped' it 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 CO<sub>2</sub>.

The author believes that it is preferable to mask the borders of the printed 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 CO<sub>2</sub> 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), 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 metals.

### 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.

**N.B.** Do not allow the processing solutions, especially bath 2, to come in contact with your skin: use print tongs or gloves.

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;

In a 100% platinum print the print-out is less vigorous, especially at low RH. Better quality may result if the more energetic, platinotype developer, 30% w/v potassium oxalate solution, is used for bath 2.

## Finishing

The print is easy to retouch using permanent watercolour pigments.

## Permanence & Stability

Platino–palladiotypes are highly lightfast and robustly resistant to all contaminants likely to arise in a normal environment.

## Summary of Platino-palladiotype Procedure

1. **Unbuffered paper:** pre-humidified to 70–80% RH. Choose side, mark up coating area
2. **Mix sensitizer:** measure and mix equal volumes of iron and platinum/palladium solutions; add Tween to ca. 0.2% if needed
3. **Coat paper:** ~1.5 cc per 10x8 in. 5 'passes' of rod
4. **Dry:** 1–2 hours at room temperature, or hot air for 10 minutes
5. **Negative:** density range ~2–2.4 in the UVA
6. **Humidify coating:** in controlled RH box (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
9. **Develop and Clear #1:** Disodium EDTA 5% for 10 minutes
10. **Rinse** in water half minute
11. **Reduce and Clear #2:** Sodium metabisulphite 2.5% 10 minutes
12. **Rinse** in water half minute
13. **Final Clear #3:** Tetrasodium EDTA 5% for 10 minutes
14. **Wash:** at least 30 minutes
15. **Drain, Dry** and press flat

## Printing in 100% Platinum

With a pure platinum sensitizer the print-out is less vigorous, the reactions are slower, and special care is needed to achieve the best print quality. The cardinal points to observe are as follows:

- The choice of paper is critical. It must contain no trace of gelatin size (see §7.6) or alkaline buffer (calcium carbonate, see §8.6). Several of the Crane's papers (Crest parchment, AS8111, Cover Natural White) work well, as do Buxton and Herschel handmade papers. Wyndstone Vellum and other 'parchmentized' papers may also give fine results.
- Newly-mixed sensitizer should be allowed to 'mature' in the dark for an hour before coating, to obtain the best  $D_{\max}$ . This need not interrupt the flow of work, because this mixed sensitizer appears to be stable for years, so a batch can be prepared in advance of printing sessions.
- A generous post-hydration (after exposure, but before immersion in the wet processing baths) will give the image the best chance to complete its print-out. 20–30 minutes over water at room temperature, or 2–4 minutes over water at 40 °C are recommended.
- If highlight detail is still deficient, or 'grain' evident due to the fibrous structure of the paper, then the first processing bath (disodium EDTA) may be replaced with the more energetic traditional platinotype developer bath of ~30% potassium oxalate (poisonous!). It may even be used hot.
- Although it is a 'cheat', adding just one drop of palladium solution to the sensitizer can improve print-out. It appears to work as a catalyst. Re-used 'developer', that may contain some palladium, probably also helps in this way.
- The judicious use of Tween 20 can be beneficial to assist the sensitizer penetrate the paper fibres and smooth out the tones. The optimum concentration depends on the chosen paper. Tween does not keep very well in dilute solution. It is best to make up a 10% solution in distilled water as stock: one drop (ca. 0.05 cc) of this per 1 cc of sensitizer gives a final Tween concentration of ca. 0.5%. Less than this may suffice.

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<sup>i</sup> Assuming a specific coating volume of 25 cm<sup>3</sup>/m<sup>2</sup> of sensitizer, of concentration 0.7 molar in ferrioxalate, complete exposure to transform all the iron to Fe(II) would release 0.025 x 0.7 = 0.0175 moles of CO<sub>2</sub> /m<sup>2</sup>. The volume of this amount of gas is 0.0175 x 22400 = 392 cm<sup>3</sup> of CO<sub>2</sub> /m<sup>2</sup> at S.T.P. The 'layer thickness' of this amount of gas is 392/10,000 cm = 0.0392 cm = 0.4 mm approximately. A separation of negative and paper by 0.1 mm is sufficient to perceptibly 'blur' an image printed on a 'light bed'.