A Step-by-Step Guide to Platinum and Palladium Printing

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There are many ways to make platinum and palladium prints. A wide range of working methods and modifications may be employed to achieve different aesthetics in these photographs, such as incorporating chemical additives in the sensitizer and/or the developer.[1] Despite the many possible variations, there are two basic ways to make platinum and palladium prints: the traditional developed-out process and the alternative printed-out process. The traditional platinum printing process, patented by William Willis Jr. (1841–1923) in 1873,[2] requires a chemical developer to complete image formation, as does the palladium process.[3] The printed-out platinum process, also called the direct-printing or water-developed method, was introduced in 1887 by Giuseppe Pizzighelli (1849–1912) and uses only water to "develop" the final image.[4] A modern version of the printed-out process, developed by Pradip Malde and Mike Ware in the 1980s and used to make both platinum and palladium prints, will illustrate this essay.[5] Although the metal image is formed in slightly different ways in each process, both are based on the light sensitivity of iron compounds. The following step-by-step guide illustrates the basic materials and methods used to make a print in platinum or palladium (platinum/palladium), or a combination of both (platinum-palladium), by the traditional developed-out and alternative printed-out processes.[6]

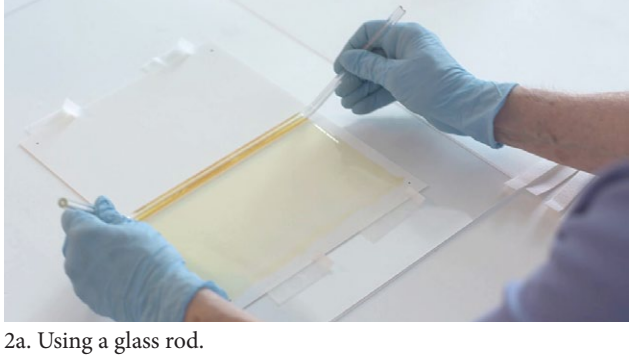
1. Sensitization

Both printing processes begin by coating the paper to make it light sensitive. The chemistry to make the sensitizer for both methods includes an iron salt (the light-sensitive component) and one or both of the platinum and/or palladium salts dissolved in water. This solution is applied to the paper in subdued light. The fact that no darkroom is required to make a platinum/palladium print is a great advantage when compared with silver processes.

The sensitizer formula for the traditional platinum/palladium print includes the following basic components in an aqueous solution: in general, 1 part of the iron salt solution is mixed with 1 part of the metal salt solution or solutions (fig. 1). The metal salts may be used individually to make a platinum or palladium print, or they can be combined to produce a platinum-palladium print (or palladium-platinum print if a greater amount of palladium than platinum is used):[7]

Figure 1. Mixing the sensitizer using 2 parts of the iron solution, 1 part of the platinum solution, and 1 part of the palladium solution.

Figure 2. Applying the sensitizer.



2a. Using a glass rod.

2b. Using a brush.

2c. The sensitizer must be allowed to dry thoroughly before exposure.

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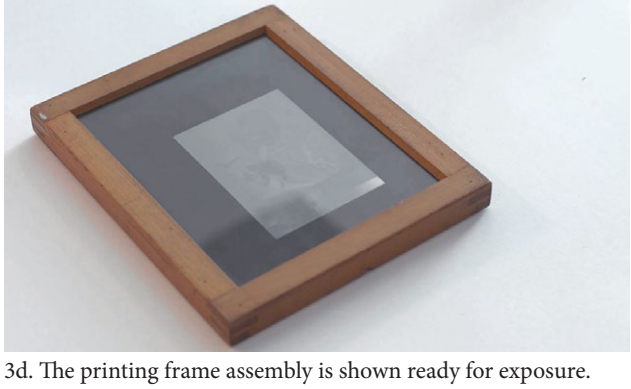
Figure 3. Positioning the negative for exposure.

3a. The negative is placed in a wooden printing frame, emulsion up, against the glass, along with a black paper mask.

3b. The sensitized side of the paper is placed in direct contact with the negative.

3c. The hinged back is held with spring-loaded metal clips.



3d. The printing frame assembly is shown ready for exposure.

sensitizer for the traditional developed-out process

- iron salt: ferric oxalate ($Fe_2(C_2O_4)_3$), 25% w/v containing excess
- oxalic acid ($(COOH)_2$), 2% w/v
- platinum salt: potassium tetrachloroplatinate (K_2PtCl_4), 18.5% w/v
- palladium salt: sodium tetrachloropalladate (Na_2PdCl_4), 14.7% w/v.

The alternative printed-out process sensitizer formula includes the following components in an aqueous solution:[8]

sensitizer for the alternative developed-out process

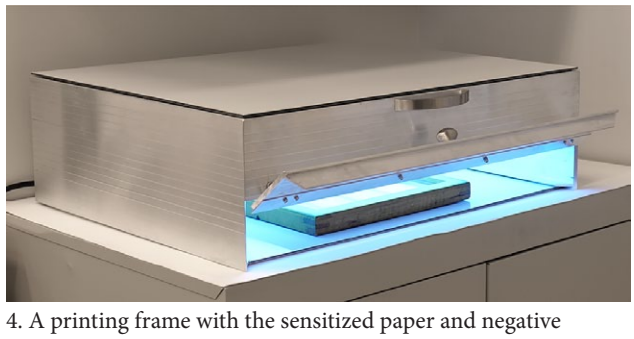
- iron salt: ammonium ferric oxalate ($(NH_4)_3[Fe(C_2O_4)_3]\cdot 3H_2O$), 60% w/v
- platinum salt: ammonium tetrachloroplatinate ($(NH_4)_2[PtCl_4]$), 25% w/v
- palladium salt: ammonium tetrachloropalladate ($(NH_4)_2[PdCl_4]$), 19% w/v.

A carefully measured amount of sensitizer solution is then applied with a brush or glass rod to the paper. The paper and applied sensitizer must then dry completely before exposure (fig. 2).

2. Exposure

Both the traditional and the alternative processes are exposed in the same manner (fig. 3). The negative is positioned on the glass of the printing frame, emulsion up. Then the sensitized side of the paper is placed in contact with the negative. This printing frame holds the negative and photo paper in firm contact against the glass using a spring-loaded hinged back.

Ultraviolet (UV) light is necessary to create platinum and palladium prints. Natural sunlight or a lamp with a high ultraviolet output will provide the light necessary for exposure. The printing frame assembly is placed under the light source (fig. 4), and during exposure the UV light reduces the ferric oxalate in the sensitizer to ferrous oxalate.



4. A printing frame with the sensitized paper and negative being exposed to a fluorescent exposure device.

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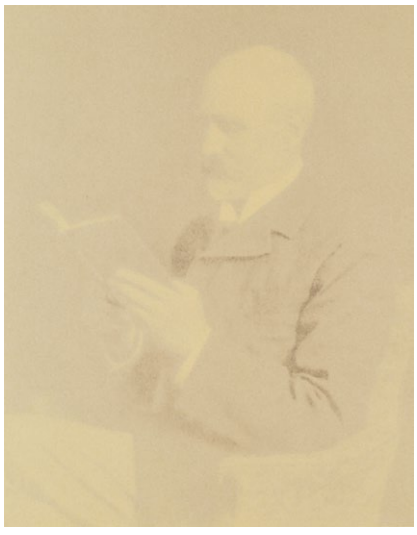
Figure 5. Inspecting a platinum print.

5a. Lifting the hinged back of the printing frame to inspect a platinum print.



5b. A partially printed-out platinum print.

3. Inspection

During exposure, the image begins to appear. The hinged design of the printing frame allows inspection of the progress of the exposure without disrupting registration between the paper and negative (fig. 5). An experienced eye can judge when the print is ready for development.

4. Development

Once the print is properly exposed, it is removed from the printing frame and is ready to be developed.

Developing a Traditional Print

The traditional process requires a chemical developer to complete the image. The exposed print is placed in a tray of developer, where it is immersed completely. While in the developer bath, the exposed iron salts react with the platinum (and/or palladium) salts in the sensitizer, reducing them to elemental platinum or palladium, or a combination of both. This reaction completes the formation of the image (fig. 6):

<u>developer for the traditional platinum print (often used for combination platinum-palladium prints)</u>[9]

- 28% w/v potassium oxalate ($K_2C_2O_4$) in water

<u>developer for the traditional palladium print (used solely for developing palladium prints)</u>

- 20% w/v trisodium citrate ($Na_3C_6H_5O_7$) + 2% w/v citric acid ($C_6H_8O_7$) in water.

Developing an Alternative Print

In the alternative process, the final image forms in the presence of water. If the sensitized paper is dried prior to exposure, water must be introduced to complete the development process. Steam is a gentle way to add the moisture required to develop the image. Paper with a low moisture content will produce a sepia-toned print (fig. 7).

If the sensitized paper is humidified (c. 75% RH) prior to exposure, the image completely develops spontaneously, producing a fully printed-out photograph. No further development is required. A print made with paper with a high moisture content produces a neutral-toned image (fig. 8).

Figure 6. An exposed platinum print.

6a. Before development.

6b. During development.

6c. After development.

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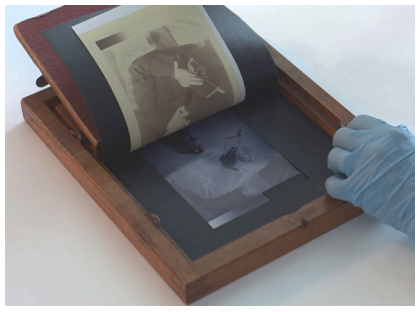
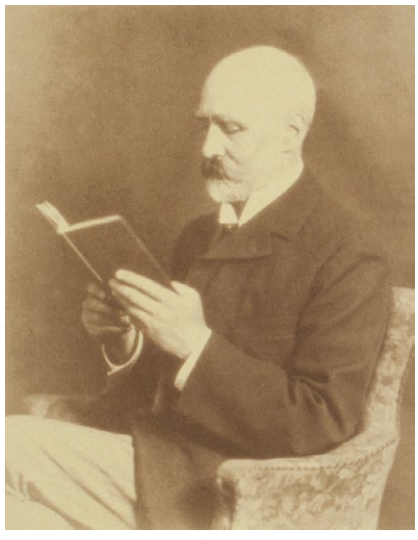
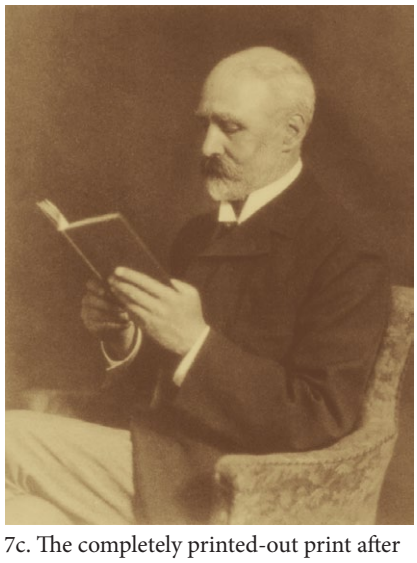
Figure 7. A platinum-palladium print made with the alternative process. The paper was dried prior to exposure.



7a. Inspecting the partially printed-out print.



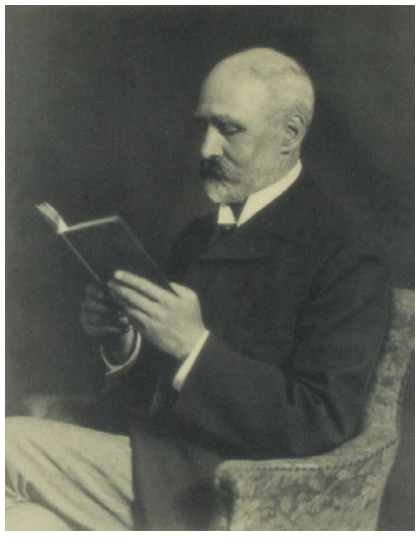
7b. The print before "water development" by steaming.



7c. The completely printed-out print after "water development" by steaming. Note the warm image hue.

Figure 8. A platinum-palladium print made with the alternative process. The paper was humidified prior to exposure.

8a. Inspecting the completely printed-out or "direct" print.



8b. The completely printed-out print requires no further development. Note the neutral image hue.

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5. Clearing, Washing, and Drying

Both the traditional developed-out and the alternative printed-out processes must be chemically cleared to remove all of the remaining sensitizer components, especially the iron salts, which are yellow in color.

During chemical clearing, the sensitizer's iron salts are converted to water-soluble complexes that are mostly removed in the clearing bath and subsequently washed away in the water baths (fig. 9). Even if the print does not appear yellow upon initial inspection, small amounts of sensitizer may remain if it is not properly cleared. Thorough clearing with fresh solutions and washing are essential to prevent any invisible iron from causing staining of the paper over time.[10]

Clearing with Traditional Methods

Traditional clearing baths for platinum and palladium prints utilized hydrochloric acid in various dilutions, but sodium citrate was recommended for palladium prints because they were susceptible to image loss in the hydrochloric acid bath:

Figure 9. Clearing the prints.

9a. The yellow sensitizer begins to dissolve in the clearing bath.

9b. After several exchanges of the clearing bath, the print is ready to be washed and dried.

clearing bath for a traditional platinum print

- 1:60 dilution of concentrated hydrochloric acid

clearing bath for a traditional palladium print

- 20% w/v sodium citrate + 9% w/v citric acid (diluted 8× with water)

  – or –

- 1:200 dilution of concentrated hydrochloric acid.[11]

Clearing with a Modern Alternative

Neither hydrochloric acid nor sodium citrate are entirely effective in making the iron compounds completely soluble. An alternative clearing agent in modern use is the chelator tetrasodium ethylenediaminetetraacetic acid (EDTA). Recent analysis shows that when used by itself, this chelator is also not completely effective in removing all residual iron compounds.[12] The photochemist Mike Ware developed a multistep clearing bath process in 1988[13] that begins with an acidic solution of disodium EDTA, which is effective in removal of ferric, Fe(III), ions, followed by a bath of sulfite to reduce any remaining Fe(III) to Fe(II), and ending with alkaline tetrasodium EDTA to remove the ferrous, Fe(II), ions.[14] The following three successive 10 minute clearing baths are recommended for a thorough clear:[15]

clearing bath for the modern alternative

- disodium EDTA ($(NaO_2CCH_2)_2NCH_2CH_2N(CH_2CO_2H)_2$), 5% w/v in water
- sodium disulfite ($Na_2S_2O_5$), 2.5% w/v in water
- tetrasodium EDTA ($(CH_2N(CH_2CO_2Na)_2)_2$), 5% w/v in water.

Platinum and palladium prints made with this modern clearing method will remain in excellent condition (fig. 10).[16]

Washing and Drying

It is essential to stress that without proper clearing, no amount of washing will remove the residual iron compounds, and they will result in staining. Recommended wash times may vary depending on the size, density, and thickness of the paper, but a 20–30 minute wash in running water is a commonly recommended starting point to properly clear prints. The prints may be hung to air-dry or held between clean blotters of pure quality, which should be exchanged until the prints are dry and flat.

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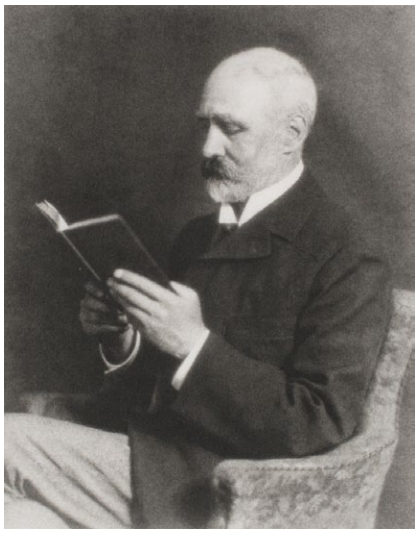
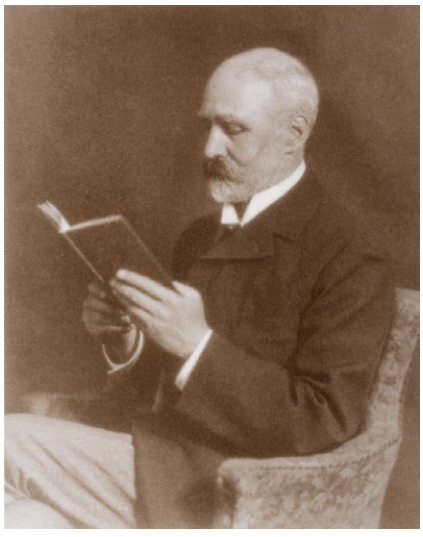
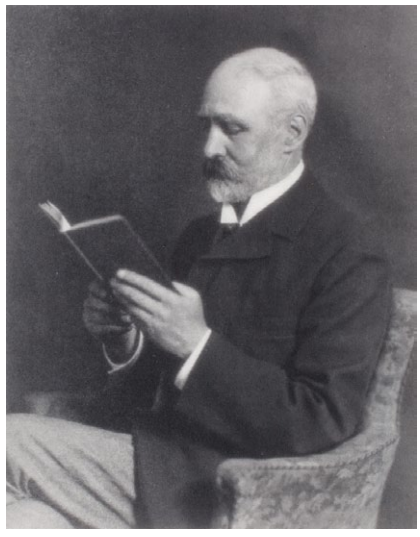
Figure 10. A comparison of three prints.



10a. A traditional developed-out print.



10b. An alternative printed-out print that was dried prior to exposure.



10c. An alternative printed-out that was humidified prior to exposure.

Notes

1. See Alice Carver-Kubik et al., "Additives Used in the Platinum Process," in this volume.

2. Willis 1873. See also Mike Ware, "The Technical History and Chemistry of Platinum and Palladium Printing," in this volume.

3. Crawford 1979, 167–72; James 2016, 309–11. Crawford and James provide easy-to-follow instructions that are based on historic recipes.

4. Gunther 1887; Stieglitz 1891.

5. Pradip Malde, "Print-Out Platinum-Palladium Printing," November 2016, Pradip Malde Photographs website, www.pradipmalde.com; Mike Ware, "The Platino-Palladiotype Process," 2014, Mike Ware Alternative Photography website, www.mikeware.co.uk. The alternative platinum-palladium process, described in this volume as the Malde-Ware process, is outlined in detail at http://pradipmalde.com/pt-pd-printing/ and http://www.mikeware.co.uk/mikeware/Platino-Palladiotype.html.

6. For further discussion of these terms, see note 1 in Pradip Malde, "Looking at a Platinum/Palladium Print," in this volume.

7. For photographers, the choice of the amount of platinum and/or palladium used in the printing process is a matter of personal artistic preference.

8. Malde, "Print-Out Platinum-Palladium Printing"; Ware, "The Platino-Palladiotype Process."

9. Neblette 1942, 695. Potassium oxalate has also been used as a developer for palladium and platinum-palladium prints. See Vasilios Zatse and Constance McCabe, "Irving Penn's Platinum-Palladium Prints," in this volume.

10. See Matthew L. Clarke, "Characterization, Degradation, and Analysis of Platinum and Palladium Prints," in this volume. See also Ware "The Platino-Palladiotype Process"; Crawford 1979, 167–72.

11. Anderson 1938, 460.

12. Clarke, "Characterization, Degradation, and Analysis of Platinum and Palladium Prints," in this volume.

13. Mike Ware, laboratory record, May 30, 1988.

14. Malde, "Print-Out Platinum-Palladium Printing"; Ware, "The Platino-Palladiotype Process."

15. Longer clearing times may be required for very thick or dense papers.

16. See Jennifer Jae Gutierrez, "Caring for Platinum and Palladium Prints: Storage and Display," in this volume.

References

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