

PLATINUM/PALLADIUM PRINTING

Introduction

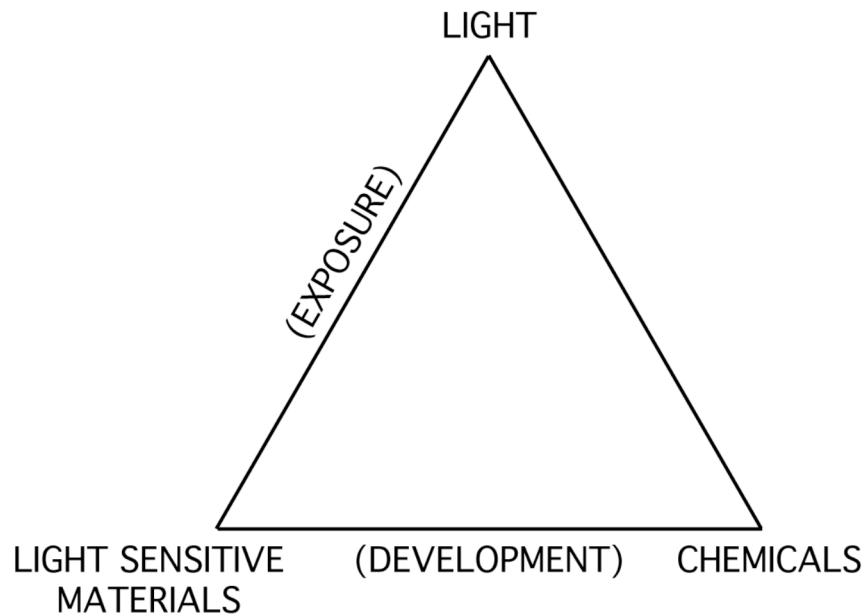
Platinum and palladium prints are known and admired for many reasons, among them a long, rich and delicate tonal scale and unmatched archival quality. Although one of the first photographic processes invented, platinum and palladium printing are rarely used by photographers today because printing on one's own can be costly in time and money. Platinum (Pt) and palladium (Pd) are similar metals which produce prints characterized by an exceptionally long tonal scale. What might be a monochromatic black on a silver print, for example, will be rendered as a series of subtly differentiated shadow tones on a Pt/Pd print. Similarly, middle and highlight tones are more delicately defined with this non-silver process. Since the prints are hand coated onto artist's quality rag paper, the image actually sits in the fiber of the paper so the texture and weave of the paper become integral to the image compared to silver prints where the emulsion layer sits on top of, rather than in, the paper surface. Platinum and palladium were titled "noble metals" by the alchemists because they were impervious to all solvents save aqua regia, The King's Water, a potent mix of concentrated hydrochloric and nitric acids. This makes the metals among the most archival available, far more resistant to light, oxidation, and chemical contamination than silver; well made prints from the mid-1800's show no fading or staining. A well processed Pt/Pd print lasts as long as the substrate it is printed on; the paper base will fall apart before the metals show any change.

There is much material available on Platinum/Palladium printing. Both historic and contemporary articles examine these two non-silver processes and the many diverse ways of working with them. A photographer has many choices available: which metal to use or, if both, in what proportion; other choices include paper, developer, clearing agents, method of applying sensitizer, method of achieving contrast control, and on and on. Some photographers find so many variables and possibilities challenging and stick with Pt/Pd printing; others find them aggravating and return to silver printing or an easier non-silver technology. What is curious about the readings, and also sometimes frustrating, is not simply that they report on many different practices, but exhort them in definitive, often authoritarian ways. One person says that hydrochloric acid must be used as a clearing agent, while another says it should never be used; one will say paper must be humidified before printing while another says humidification is overemphasized. As such, this manual presents my technique of Pt/Pd printing, which is not to say it is the best technique, but the one which I prefer. My preference is based on many factors: print quality, cost, convenience, work methods, etc. Eventually, one must pick and choose which advice to consider, test, and follow. However one responds to the exhortations about how to print with Pt/Pd, one must realize that it is a process with many variables and that to succeed with it demands, at the least, precise and repeatable procedures and disciplined work habits.

The Process - An Overview

"In the platinum process, paper is sensitized with ferric oxalate and potassium chloroplatinite. On exposure to light, the ferric salts are reduced to the ferrous state. When the paper is placed in a potassium oxalate developer, the new ferrous salts are dissolved and in turn reduce the platinum in contact with them to the metallic state. The print is then cleared in hydrochloric acid to eliminate the ferric salts remaining in the paper. The image that is left consists of metallic platinum in a finely divided state." (Keepers of Light, p. 167)

Say what? Well, in order to understand that definition and to understand the many other variables to be discussed, I suggest the following Holy Trinity of Photography.



All photographic processes, by definition, require that light strikes a light sensitive material (the exposure) which is then processed in chemicals (the development). All photographic processes can be explained by the Trinity diagrammed above. Whether one is working with color negatives or slides, black and white negatives or Polaroids, Cyanotypes or Liquid Light, this Photographic Holy Trinity gives us a scheme into which we can place the new words, procedures and techniques of any photographic process and make them understandable. One need not be a physicist nor a chemist to understand the process, but a little understanding of the physical and chemical processes in Pt/Pd printing will be invaluable in learning why certain procedures work as they do and how to gain control over the medium. We will first discuss the print material in terms of the Trinity, then the film material.

LIGHT: THE Pt/Pd PRINT

When we discuss light, we must discuss it in terms of its **quantity** and **quality**. A Pt/Pd print requires a tremendous quantity of light to expose it. The sun has for over a century been used for exposing Pt/Pd prints because it provides such a huge quantity of light. An enlarger, by comparison, produces a very small quantity of light, not nearly enough to expose a Pt/Pd print. Furthermore, the quality of light needed to produce a Pt/Pd print is very specific: ultraviolet (UV) light must be used. The sun is rich in UV light, while an enlarger isn't. So, an enlarger delivers neither the correct quantity nor quality of light to expose a Pt/Pd print; that's why it is a contact printing process only. One must make a negative of the same size as the desired print and expose it to a light source rich in UV light. Many people still print by the sun, while others use specially designed printers which produce a high quantity of the right quality (UV) light. These printers can be made easily and relatively cheaply (described later).

LIGHT SENSITIVE MATERIAL: THE Pt/Pd PRINT

Pt/Pd prints are often identified as iron salt prints because the light sensitive metal in a Pt/Pd print is actually an iron compound, specifically ferric oxalate (FeOx). Cyanotype and Van Dyke are also iron printing methods. In all these methods the iron salt is what responds to exposure to UV light. The FeOx, upon exposure to light, reduces to ferrous oxalate and it is later, in development, that the other metals, platinum and palladium, attach themselves to the exposed iron particles to make the Pt/Pd print. In making a Pt/Pd print, the photographer coats a piece of paper with a sensitizer composed of FeOx and

metal (Pt, Pd, or a combination of both). It is not technically an emulsion, since no emulsifiers are used. The absence of emulsifiers allows the sensitizer solution to soak into the fibers of the paper which accounts for much of the image quality of a Pt/Pd print: the image sits in the paper, not on it. More exposure means more reduction and, as with silver printing, more density.

There are two ways to achieve contrast control in Pt/Pd printing: by changing the sensitizer and/or the developer. Sensitizer changes will be discussed in this section; developer changes will be discussed later. Contrast control with the sensitizer is made possible by the use of two different ferric oxalate solutions. The first FeOx solution (called A or no.1) has ferric oxalate only; the second FeOx solution (called B or no.2) has added to it a small amount of Potassium Chlorate, which acts as a chemical reducing agent. As one changes the proportion of FeOx 1 to FeOx 2, one changes the contrast of the print material; the greater the proportion of FeOx 2, the greater the amount of contrast. As with silver printing, we choose the paper contrast or grade primarily in response to the negative contrast (though aesthetic choices might alter that). If a negative is very contrasty in silver printing, we have to respond by printing on a soft paper: a grade 0 or 1. On the other hand, if a negative is soft, we have to print on a harder, more contrasty paper, like a 3, 4 or even 5. The same principle applies to Pt/Pd. Softer negatives require a more contrasty sensitizer (less FeOx 1, more FeOx 2) while harder negatives require a less contrasty sensitizer (more FeOx 1, less FeOx 2). The total amount of drops of iron solution stays the same; what is changed is the proportion of FeOx 1 to FeOx 2.

The chart below shows how one would mix the sensitizer differently in response to different negatives. This chart shows the drops necessary to coat a 4x5 inch print. With larger prints, the total number of drops increases, but the proportions stay the same. For example, an 8x10 print equals four (4) times the area of a 4x5 print so 4x more sensitizer is needed. A sensitizer for a negative of "normal" contrast for an 8x10, therefore, would need 16 drops FeOx 1, 16 drops FeOx 2 and 32 drops of Pt/Pd. *(Note: This chart is designed for beginners. It uses slightly more sensitizer than is generally called for to enable the beginner printer to coat more easily by using more sensitizer. After one is practiced at coating, he or she can use the chart printed later to save \$\$.)*

NEGATIVE CONTRAST	FeOx Sol. 1	FeOx Sol. 2	PT/PD Sol. 3
Extremely High	8	0	8
Very High	7	1	8
Quite High	6	2	8
Touch Contrasty	5	3	8
Normal	4	4	8
Touch Flat	3	5	8
Quite Flat	2	6	8
Very Flat	1	7	8
Extremely Flat	0	8	8

(Note: H2O2 can also be added to the sensitizer in small amounts to increase contrast: only 1 or 2 drops in a 4x5 mixture will have a noticeable effect. Contrast control with the developer will be discussed later)

PRINTING WITH STEP TABLETS

Using a small Stouffer step tablet while printing allows one to compare the print densities with the step tablet densities and make adjustments accordingly. Each step in a step tablet is equivalent to 1/2 stop or 1/2 Zone.

In Pt/Pd printing, expose for the shadows and adjust contrast for the highlights.

Both Shadows and Highlights are Too Dark

Compare the shadow area in the print to the shadow area in the step tablet. To lighten the print one step (ie 0.15 lighter) reduce printing time 1/2 stop or 33%. Contrast mixture does not change.

Both Shadows and Highlights are Too Light

Compare the shadow area in the print to the shadow area in the step tablet. To darken the print one step (ie 0.15 darker) increase printing time 1/2 stop or 50%. Contrast mixture does not change.

Shadows are Good, Highlights are Dark

Compare the highlight area in the print to the highlight area in the step tablet. To make a print where the shadows stay the same, but the highlights lighten one step (ie 0.15 lighter) use a *higher contrast mixture*. To compensate for the slight loss of printing speed, increase printing time 10%.

Shadows are Good, Highlights are Light

Compare the highlight area in the print to the highlight area in the step tablet. To make a print where the shadows stay the same, but the highlights darken one step (ie 0.15 darker) use a *lower contrast mixture*. To compensate for the slight increase of printing speed, reduce printing time 10%.

Shadows are Dark, Highlights are Good

Compare the shadow area in the print to the shadow area in the step tablet. To make a print where the shadows lighten one step (ie 0.15 lighter), but the highlights stay the same, decrease the exposure time by 1/2 stop or 33%. To keep the highlight areas where they are, use a *lower contrast mixture*.

Shadows are Light, Highlights are Good

Compare the shadow area in the print to the shadow area in the step tablet. To make a print where the shadows darken one step (ie 0.15 darker), but the highlights stay the same, increase the exposure time by 1/2 stop or 50%. To keep the highlight areas where they are, use a *higher contrast mixture*.

CHEMICALS: THE Pt/Pd PRINT

As mentioned above, the exposure of the print to UV light causes the ferric oxalate to be reduced to ferrous oxalate. Later, in development, the newly formed ferrous oxalate reduces the platinum or palladium salts to the metal stage; ferric oxalate will not reduce Pt/Pd salts, only ferrous oxalate will, hence the need for the exposure stage to reduce the iron salts and the development stage to reduce the metal salts. Pt/Pd prints are developed to completion; different paper/developer combinations require different development times, but usually between 1 and 2 1/2 minutes is enough. Once the development is complete, the print must be cleared, a step which insures that the unused iron and metal salts are

removed from the print so all that remains after a print is cleared and washed is finely divided platinum and/or palladium metal. The tremendous archival properties of the print come as result of many factors. First and foremost is that the the well processed print contains only platinum and/or palladium metals which are extremely durable. No other metals or chemicals remain which would deleteriously affect the image. 100% rag papers are typically used as a substrate (more later) to insure the paper is archival as well. Also, the process is blessed since fixer (hypo) is never used; residual fixer is difficult to wash from a print and a major culprit in shortening a gelatin silver photograph's life. Free from fixer, a Pt/Pd print is easier to clean and will last longer as result.

A variety of chemicals can be used to develop a Pt/Pd print: ammonium citrate, sodium citrate, potassium oxalate. Each developer has different characteristics; they vary in speed, color, and contrast, but are equally archival. Developers also change when used at different temperatures and with different papers. A heated developer, for example, will increase in speed and become warmer in color than the same developer at room temperature. As mentioned before, changes in contrast can be made by changing the sensitizer and/or the developer. Additives can be used to change the contrast of the developer, a procedure to be used in addition to or in lieu of changing contrast by varying the proportions of FeOx 1 to FeOx 2. With many developers, a 3% mixture of hydrogen peroxide (H₂O₂) can be added to make developers increasingly contrasty. 10ml of 3% H₂O₂ (drugstore variety) added to a liter of developer increases its contrast approximately a grade. With use, the H₂O₂ loses strength and the contrast of the developer eventually returns to normal. Sodium Dichromate also acts as a contrast agent, but only with Potassium Oxalate developer; it is more stable than H₂O₂ as a contrast agent. A 50% solution of Sodium Dichromate (ie 50 gm Sodium Dichromate to 100ml hot H₂O) is added to Potassium Oxalate developer at a rate of 5 drops per liter to move the developer a contrast grade. For example, 5 drops in a liter of straight developer increase its contrast one grade while 10 drops will increase it two contrast grades.

Several chemicals are commonly used for the clearing baths. In all cases, three (3) clearing baths are used with 5 minutes in each bath. This follows the logic of double fixing a silver print where the first fixing bath does most of the work, but a second, fresher fix bath is used to guarantee the print is completely fixed. Similarly, a Pt/Pd print goes into three successive clearing baths, all made identically; the first bath does most of the work, while going through a second and third bath guarantees the print will be completely free of unused iron and metal compounds and therefore archival. Common clearing agents are hydrochloric acid, citric acid, oxalic acid, EDTA (a chelating agent with a loong name), and Kodak Hypo Clear (which contains several of the previously mentioned clearing agents). One's choice of a clearing agent depends on personal choice to a degree -- for example, I don't want to work with hydrochloric acid, ever, even a mild solution -- and also the metal and paper used. For example, palladium can be bleached slightly by hydrochloric acid, but platinum can't. Crane's Platinotype paper, as another example, clears well with many different clearing agents, while Arches Platine paper is more stubborn to clear: citric acid works well, but EDTA does not. The choices one makes, therefore, for the developer and clearing agent depend on many factors, including, but not limited to, one's personal choice for what he/she wants the print to look like and how he/she wants to work in the darkroom, and what works best technically. Only experimentation with different metal/paper/chemical combinations will show a photographer all the possibilities available so that he or she may determine what choices to make and procedures to use. After clearing the print in three baths, it is washed for 25 minutes in an archival washer, then dried face up on a fiberglass screen. A print takes many hours to dry and undergoes a significant dry-down effect, darkening on drying approximately 10-12% and, furthermore, losing local contrast in the low values. Dry down effect must be attended to closely with a Pt/Pd print.

PAPER: THE Pt/Pd PRINT

Much has been said in the literature about the visual differences between platinum and palladium: Pt is

cooler and more contrasty than Pd, while Pd has a higher Dmax and is also much cheaper. Less has been said about the way images can change drastically in color and tone as result of paper/developer combinations (more on paper later). Pure palladium prints can be made to look very similar to pure platinum prints given the right paper/developer combination (and at about 1/4 the cost).

Since a Pt/Pd image literally sits in rather than on top of the paper then the characteristics of the paper are integral to the image. Paper color, surface and texture all affect the look of the final print. First, the paper must be able to withstand wet times of nearly 45 minutes. Second, to insure a Pt/Pd print's archival properties, the paper should be 100% rag. Third, some amount of surface and/or internal sizing is necessary; the Pt/Pd sensitizer needs to absorb into the paper fibers, but not so far that it is not exposed to the UV rays. Ideally, the paper's pH should be neutral or slightly acidic, a condition difficult to find since papers are becoming increasingly alkaline to meet the EPA manufacturers' standards. Lastly, a paper without brighteners is preferred. However, these conditions don't guarantee a paper will work with Pt/Pd. For example, I once purchased a Lanaquarelle paper based on a description which guaranteed the paper was 100% cotton, pH neutral, smooth surfaced (hot pressed), and surface and internally sized. By description it sounded ideal and I liked the look of its surface and its cool color. And printing was a disaster; the paper was unusable. Currently, two papers are being made specifically for the Pt/Pd process: Platinotype from Cranes Paper and Platine from Arches. Other papers which have worked include: Van Gelder Simoli Japon, Saunders Waterford, Arches Aquarelle, Fabriano Artistico and Fabriano Uno.

Speaking of personal choices, my printing procedure is as follows. I coat Arches Platine paper with a Pd/Pt sensitizer (3:2). I use more FeOx than metal: a 4x5 print, for example, is coated with 6 drops FeOx Sol.1, 3 drops of Pd, and 2 drops of Pt. I control contrast not with the sensitizer, but the developer, specifically Potassium Oxalate developer with Sodium Dichromate as the sole contrast agent. I use Kodak Hypo Clear for three clearing baths of 5 minutes apiece. Processing is done in a Jobo drum at 25rpm. After 25 minutes in an archival washer I dry the prints face up on fiberglass screens and then soak each for one minute in an 6% solution of Liquitex Acrylic Gel Medium which increases the Dmax and tonal separation, cools the print color slightly, and also gives the print a slight amount of glossiness.

SUPPLIERS

Bostick & Sullivan, PO Box 2155, Van Nuys, CA, 91404, 818-785-4130, 818-785-5857 (fax)
-Full Range of Pt/Pd Supplies, incl. Platinum, Palladium, Ferric Oxalate, many developers and papers

Universal Light Source, 1553 Folsom St., San Francisco, CA, 94103, 415-864-2880
-UV fluorescent style light bulbs (buy Super Actinic 420nm bulbs)

BOOKS

The New Platinum Print by Richard Sullivan and Carl Weese, available through Bostick & Sullivan

Outline for Platinum/Palladium Printing, Dick Arentz, 1640 N. Spyglass Way, Flagstaff, AZ. 86004

Recipes

Ferric Oxalate: The added EDTA and Oxalic Acid will add speed and shelf life to the ferric oxalate. This formula is for FeOx Sol.1; for #2 add .33 gms. potassium chlorate for Pt, .66 gms. for Pd.

27.1 gms B&S FeOx powder
4.8 gms Oxalic Acid
1.6 gms EDTA
100 ml H₂O

To mix, I usually boil filtered water (in a pan NOT used for cooking) and add it to the dry chemicals. If they precipitate out at a later date, I place the bottle, cap off, in a microwave for about 45 seconds on high to heat the solution, then shake it to redissolve the chemicals. Wait for the solution to cool before you use it.

Developers: (See p.4 for info on developer additives to control contrast)

Potassium Oxalate: 250 gms. per liter
(for warm tones try 180 gms. potassium oxalate, 60 gms. phosphate monobasic per liter)

Sodium Citrate: 266 gms. sodium carbonate, 162 gms. citric acid, 1440 ml. H₂O

Ammonium Citrate: 250 gms per liter

Clearing Baths: (Different baths for different papers; need to experiment)

Kodak Hypo Clear: Use as directed

Oxalic Acid: 50 gms per liter

Phosphoric Acid: 25 ml per liter

EDTA tetra sodium: 15 gms per liter

Sodium Sulfitite: 15 gms per liter

Enlarged Negatives/Printing

Eric J. Neilsen, 7910 Treehouse Lane, Apt 1095, Dallas, TX 75231, 214-378-8383

Doug Munson, Chicago Albumen Works, PO Box 805, Housatonic, MA, 01236, 413-274-6934

Internet Stuff

The Internet is a tremendous resource for Pt/Pd printers. There is a listserve group dedicated to Alternative Photography; its like a pen pal network with about 600 members. Once you subscribe you will receive between 10-30 letters a day from around the world about all sorts of topics in the generic category of alt-photo which include Pt/Pd, Albumen, Cyanotype, Bromoils, etc. If you post a comment or question you can expect quite a large response. Many Pt/Pd experts participate: Dick Sullivan (of Bostick and Sullivan), Luis Nadeau, Mike Ware. Not to mention William Laven.

The administrative address is: alt-photo-process-request@sask.usask.ca **To subscribe**, simply send an email with the command "subscribe alt-photo-process-l" (without quotation marks, it ends with

the letter “l”; it’s not the number one) as the only text in the message box. You’ll start getting letters the same day. To unsubscribe, use the following command: unsubscribe alt-photo-process-l

Remember that web pages come and go. Given that caveat, some good web pages at the time of this writing are:

- www.platinotype.com (My page)
- www.aperture-photo.com/site/platinum/platinum.html (info from Aperture)
- www.collectorsguide.com/sf/g171.html (The Platinum Gallery Collector’s Guide)
- www.metalsmiths.com/platinu.html (info on Platinum from a metallurgist)
- www.a1.nl/phomepag/markerink/pyrofaq.htm (info on Pyro processing)
- www.busdir.com/ericneilsen/index.html (page of Eric Neilsen, Pt/Pd printer)
- www.duke.usask.ca/~holtsg/photo/faq.html (Alt-Photo faq)
- www.primenet.com/~dbarto/lnadeau.html#A0 (Luis Nadeus’s page)
- www.bostick-sullivan.com/toc.htm (Bostick & Sullivan’s page)
- www.nfinity.com/~mdmuir/ (Maximum Monochrome)
- www.mikeware.demon.co.uk/ (Mike Ware’s page)
- www.kerik.com (Kerik Kouklis’s page)
- www.hazards.com (searchable database for MSDS’s [Material Safety Data Sheet])
- <http://www.apug.org/forums/forumdisplay.php?f=42> (APUG forum on alt. processes)

Chart for Practiced Coaters (Use this chart when you are a confident coater. It uses less solution than the one earlier in the manual)

<u>NEGATIVE CONTRAST</u>	<u>FeOx Sol. 1</u>	<u>FeOx Sol. 2</u>	<u>PT/PD Sol. 3</u>
Very High	6	0	6
Quite High	5	1	6
Touch Contrasty	4	2	6
Normal	3	3	6
Touch Flat	2	4	6
Quite Flat	1	5	6
Very Flat	0	6	6

Author

William Laven, B.A., EdM., completed an MFA in photography at San Francisco Art Institute in 1991. He has taught photography for decades at schools and workshops throughout the country, including San Francisco Art Institute, University of California at Davis, California College of Arts Extension Program, UC Santa Cruz Extension Program, Coupeville Arts Program and the Oregon College of Arts and Crafts. He currently teaches workshops and tutorials in Pt/Pd printing out of his studio/darkroom in San Francisco. Contact him at: 1931 23rd Street, San Francisco, CA, 415-647-9292 (voice), 415-647-9294 (fax); wmlaven@platinotype.com; www.platinotype.com