

## What (I Think) I Know About Platinum/Palladium Printing

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Platinum and palladium are two metals with similar chemical properties which hold a special place in the history of photographic imaging. When reduced to pure metal, as they are in a photographic print, they are nearly inert to UV light and atmospheric pollutants. Thus a pt/pd print is extremely archival. Better yet, pt/pd can form images in a pleasing variety of tones ranging from warm chocolate brown to nearly neutral blue/black. A practical method for making pt/pd prints was invented in the 1870's by Willis and it was considered one of the premiere printing methods until WWI when the use of platinum for munitions priced it out of the photographic market. Silver-gelatin printing papers, with a printing speed that allowed enlargement, took over and the art and practice of pt/pd printing nearly died out.

Pt/pd has a reputation for being a difficult medium in which to print. That used to be the case, but is no longer true. Both metals, when used without any contrast agent, produce emulsions that are very low contrast. Printing on such an emulsion requires a correspondingly high contrast negative. Making an analog, wet darkroom negative correctly tailored to a pt/pd emulsion is a tricky business. Not only must the negative be pushed to the correct high contrast, it must also be tailored to give good detail in both the shadows (which tend to block up easily) and the highlights. If you look at vintage platinum prints from around the turn of the century, it looks like many printers just gave up on trying to achieve a really rich black and instead printed for the extensively shaded high tones that pt/pd can yield. These prints can look very soft and beautiful but completely lack anything you could call black. When pt/pd printing began to be revived after WWII, photographers such as Irving Penn would print with multiple negatives, one for shadow detail, one for highlights, in order to print the entire range that pt/pd is capable of displaying. It can be difficult to hit the precisely correct contrast with an analog negative. To avoid having to go back and remake the negative, printers worked out a number of ways to alter the contrast of the pt/pd emulsion itself. A commonly used

contrast agent was potassium chlorate. Unfortunately, in addition to increasing emulsion contrast, this chemical slowed printing speed and made the print look grainy. A better contrast agent is the recently re-discovered chemical disodium chloroplatinate (often abbreviated as NA2). In small amounts this platinum salt strongly alters contrast but causes less grain (though it still causes some). The result of all this is that good printers had a variety of approaches to making the best negative or combination of negatives. And they also had preferred potions for fine tuning emulsion contrast. This is why pt/pd printing got the reputation for being a tricky printing medium.

The introduction of digital negatives for pt/pd printing has completely changed this situation. It is now easy to set the contrast range of a digital negative to exactly the contrast desired. Once set, that contrast can be accurately reproduced, negative after negative, with no variation. Likewise, a digital negative can readily be produced with the desired tonal separation in both shadows and highlights. In other words, it is now possible to precisely tailor a digital negative to a particular pt/pd emulsion. If the print does not come out right, you go back and remake the negative, you do not fiddle the emulsion. As a consequence, the actual printing process becomes nearly mechanical. Expose for the standard time, develop in the standard developer, clear, wash, and dry.

Traditionally, many printers preferred to use a mixture of platinum and palladium. Platinum is a bit more contrasty and gives a somewhat cooler tone. Palladium is softer and gives a warmer tone. Also, palladium used to be cheaper so it kept the cost down. In this workshop we will use straight palladium. This yields a very soft emulsion with a rich warm tone I happen to like. It is just as easy to make a digital negative for pure palladium as for any pt/pd mixture. Palladium chloride is not very soluble in water so we must add a co-salt to get it to dissolve. The co-salt can be any of several salts, such as sodium chloride, lithium chloride, cesium chloride, etc. Somewhat by historical chance I started using lithium chloride as the co-salt, learned to like the results, and have never really worked with any of the others. According to the literature they all have subtly different colors and printing properties and you might want to experiment with them someday.

Palladium in solution is completely insensitive to light (UV or visible). To make it light sensitive, it is mixed with ferric oxalate. Exposure to UV light activates the ferric oxalate, releasing electrons which reduce palladium to pure metal which is then trapped in the paper fibers to form the image. Unfortunately, a low level of palladium reduction often occurs even in the absence of UV light, especially with older ferric oxalate solutions. This shows up as slightly fogged highlights. To prevent such fog I normally add a small amount of the contrast agent disodium chloroplatinate (NA2) to the palladium/ferric oxalate emulsion mix. This is just enough NA2 to keep the highlights white without materially altering the overall contrast of the print.

Here is the emulsion mixture I normally use to coat an image area of about 15 x 18 inches:

10% lithium chloropalladite	3 ml (3.5 g LiCl, 5 grams PdCl <sub>2</sub> , 50 ml water)
27% ferric oxalate	3 ml (13 g ferric oxalate, 50 ml water)
2% NA2	0.15 ml (3 ml 20% NA2, 27 ml water)

Coating of large areas (over 8x10 inches) is done with a brush. In fact, now that I know how to use one, I coat all sizes with a brush. Some people swear by brushes with extremely soft bristles, such as the 2 inch brush sold by Jack Richeson (Google it to find an internet seller). I find, however, that with proper technique less expensive brushes with stiffer bristles work just as well. I use a 2 inch brush sold by Dan Smith which I have modified by using a razor blade to cut off some of the bristles from both sides (hopefully this prevents the brush from absorbing so much expensive emulsion). The secret to a smooth coating is to have enough liquid on the paper. If there is enough liquid the coating will level itself and become very smooth. If the above recipe is not leaving enough liquid on a 15x18 inch print (this happens in the hot summer sometimes) you can add at least another milliliter of water with no bad effect on the final print.

My standard paper is Arches Platine which is available from Dan Smith. Many, many other papers can be used but I keep coming back to Platine. The area to be covered with emulsion is outlined with a light pencil line, then the entire emulsion mix is dumped

into the center of the area. The brush is first used to follow the pencil lines and outline the image area, then liquid is quickly brushed over the entire central area. Next the liquid is brushed left to right in long smooth strokes, then top to bottom in a series of long strokes. At this point you must judge if there is too much liquid on the paper. If there is too much liquid and puddles are present, the brush should be briefly touched to a paper towel at the end of each stroke to get rid of some of it. The ideal is to reach a state, after 2 - 3 complete sets of brush passes, in which the surface is quite wet but not obviously puddled. At this point you let the paper sit for about five minutes and the remaining liquid will even out and start drying to a completely even, rich orange brown coating.

Palladium emulsions can be coated under normal tungsten room illumination. Fluorescent fixtures emit some UV light and should be avoided.

I used to dry the coated paper with a hot hair dryer but I now realize that was barbarically poor practice. An emulsion containing lithium chloropalladite can yield a deep velvety black, but to do so it must have a certain amount of humidity in the emulsion when it is exposed (to what degree this is true for palladium dissolved with other of the possible co-salts, I do not know). Overdrying results in weaker brownish blacks and can even lead to tonal reversal (solarization) in the darkest tones. After reading the literature I have settled on this relatively simple method for controlling emulsion humidity and obtaining reproducible deep blacks.

I set up a small fan so that it blows room temperature air across the drying table. I also set up an inexpensive greenhouse humidity meter in the path of the fan. Once the wet liquid sheen is gone from the coated paper I lay it in the path of the small fan for 5-10 minutes. During that time it becomes dry to the touch but does not appear to overdry. I expose the coated paper as soon as it is dry enough that the negative will not stick to it.

Needless to say, one should use the same humidity control when making step tablet test prints to derive correction curves.

To expose a palladium emulsion you need a source of UV light in the 340 nanometer range. Traditionally that source was sunlight. However, in the Northwest an

artificial source is much more practical. The most practical and economic source is a bank of UV emitting fluorescent tubes which can either be purchased ready made or assembled with a bit of handycraft. The best source is a graphic arts plate burner such as those that were made by Nuarc. These machines are especially valuable because they come with a vacuum bed that ensures tight contact between negative and coated paper. Since they are no longer used by the printing industry these machines can often be found rather reasonably on Ebay. However, they are large industrial machines. They require 220 voltage and moving them and finding space for them can be a problem.

Whatever the exposure source, it is necessary to determine the basic printing exposure. This is defined as the minimum exposure needed to print maximum black through the clear Pictorico substrate. To determine the basic exposure time, place a clear piece of Pictorico so that it half covers a coated piece of paper. Then perform a series of exposure tests to determine how much UV it takes to make the boundary between the covered and uncovered sides just disappear. For this test it is essential that the coated paper not be overdried. Overdrying will lead to solarization of the dark tones causing a considerable overestimate of the true basic exposure time.

The exposed print is developed in a nearly saturated solution of potassium oxalate (250 g per liter of water). Place the exposed print in a dry tray and pour the developer from a wide mouth vessel so that it rapidly covers the print in one smooth pour. An image will come up immediately. But let the print sit in the developer for at least a minute to allow maximum black to appear. Then pour the developer back into the pouring vessel and rinse the print with water. Then cover the print with more water and let it sit for five minutes or so. The goal from here on is to get rid of all ferric oxalate and unexposed palladium salts from the paper. Anything that can be washed off in this initial water soak will be that much less to contaminate and exhaust the later clearing baths.

I now realize that I am fortunate in Seattle that the city water supply is not alkaline. Therefore, the initial rinses after development can be done with tap water. In other parts of the country it may be necessary to do the initial rinses in a weak acid (such as 5% citric acid). As I understand it, alkaline conditions causes ferric oxalate to precipitate in

the paper fibers and it becomes nearly impossible to clear it out. So check you local water supply.

Potassium oxalate developer can be used over and over in spite of the fact that it will become green black with dissolved salts. Occasionally I will add some potassium crystals to keep it near saturation and make up more if the volume runs low. Also, it wants to remain a bit on the acid side, definitely not alkaline.

There are numerous recipes for clearing baths. The one I use is 2 tablespoons of sodium sulfite plus 4 tablespoons of EDTA per 4 liters of water. I make two of these baths. The rinsed print goes in the first for 5-10 minutes, then into the second for another 5-10 minutes. When the first bath gets to looking a bit green I replace it with the second bath and make fresh second bath. After the two clearing baths the print gets 4 water baths of 5-10 minutes each and then is placed on a plastic window screen to air dry.

At the last APIS meeting in SantaFe I asked the assembled experts how they know when prints have completely cleared. The answer seems to be that there is no objective measurement that tells you when clearing is complete. So, I clear until all traces of yellow disappear and then I clear a bit more until it feels good. The same goes for washing out the clearing baths.

I do not dry mount palladium prints. Instead I hinge them on a slightly larger piece of 4-ply mat board and I leave a 1/4 inch space between the print and the glazing when framing the print.