PHOTOGRAPHERS'
FORMULARY

PHOTOGRAPHERS' FORMULARY PALLADIUM PRINTING KIT

CATALOG NUMBER 07-0007 CONTAINS 15 ML 15% PALLADIUM SOLUTION
CATALOG NUMBER 07-0009 CONTAINS 30 ML 15% PALLADIUM SOLUTION

Directions for mixing and using Formulary Palladium Printing kits containing 15 ml 15% Palladium Solution, or 30 ml 15% Palladium Solution:

Palladium salts are not light sensitive; therefore, in making a palladium print, the paper is coated with a mixture of Sodium Tetrachloropalladate and light-sensitive Ferric Oxalate. The paper is then exposed by contact printing, developed in Potassium Oxalate, and finally cleared with a dilute solution of Citric Acid to remove the iron salts.

The mechanics of printing with palladium and platinum are very similar; therefore, these directions are almost identical to Formulary's Platinum Printing directions. However, there are some differences in the appearance of the prints and in the chemistry used to produce the prints.

Palladium prints have almost the same scale, richness, and delicacy as do platinum prints but are warmer and have a smoother tone. Palladium prints are warm-black to sepia in tone while platinum prints tend to be neutral-gray. Under certain conditions, palladium prints, unlike platinum prints, will solarize.

In regards to chemistry, palladium is less sensitive to contrast control with potassium chlorate than is platinum. Therefore, twice as much chlorate is used in the preparation of the Sensitizer B for palladium printing. Also, palladium metal can be etched from the print if the clearing solution contains too much Citric Acid. The instructions for the preparation of both of these solutions are given later in these directions.

Platinum and Palladium printing is an art. These instructions are intended only as a starting point. In preparing these instructions, we have relied upon the following resource materials:

Tice, G., "Processes: Palladium and Platinum", Modern Photography (March, 1981) page 80.

Rexroth N., “The Platinotype”, Violet Press, 1977. Reprinted with permission by Photographers' Formulary.

Crawford, W., *The Keepers of Light*, Morgan and Morgan, Dobbs Ferry, New York, 1979, pp. 167-175, Formulary Cat. No. 08-0070

Wall, E.J., and Jordan, F.I., (Revised by Carroll, J.S.), *Photographic Facts and Formulas*, Prentice-Hall Inc., Englewood Cliffs, NJ, 1976, Chapter 13.

Shillea, Thomas, *Instruction Manual For The Platinum Printing Process*, highly recommended. Formulary Cat. No. 08-O025

CHEMICALS CONTAINED IN THIS KIT

This kit contains all the chemicals you will need to make palladium prints.

CHEMICAL	AMOUNT
Arrowroot starch	20 g
Ferric Oxalate Sensitizer A	30 ml
Ferric Oxalate Sensitizer B	30 ml
Citric Acid	30 g
Potassium Chlorate	.26 g
Palladium Salt solution, 15%	15 ml or 30 ml
Potassium Oxalate	227 g

ADDITIONAL EQUIPMENT NEEDED

The kit does not contain the paper you will need for printing, nor the following special equipment not usually found in a darkroom:

Camel-Hair Brush
Hair Dryer
Plywood Board
Ultraviolet Light Source
A small mixing container
(such as a jigger glass)
Split-Back Print Frame

THE NEGATIVE TO BE PRINTED

A palladium print is made by contact exposure. Therefore you will need a negative of the exact size of the final print you wish. The best negatives are obtained using a view camera. If you have only 35-mm or 2 1/4 inch negatives, then you must make a larger negative using. for example, a direct positive duplicating film.

The negative should have good separation of detail in the shadows and a long density range. Best results are obtained if the density range of the negative is between 1.3 and 1.5. A good rule of thumb is that if the negative gives a good print with contrast paper grade #1, it will print correctly with the "average print mixture." (See 'Mixing the Solutions.")

PAPER

The paper that you choose will have a dramatic effect upon the image that you obtain. The texture, the contrast, and the tonality; are all affected by the paper. Poor results are obtained with inexpensive wood papers. Pure linen paper (100% rag) is best. Watercolor and etching paper are satisfactory. Bristol papers seem to have too hard a surface for palladium printing. (The palladium falls off during development.) Use only single-ply paper - two or three ply papers separate during the washing steps.

The quality of paper varies from manufacturer to manufacturer, and possibly even from box to box labeled with the same lot number. For consistent results, select a
negative and use it as your standard. When using new paper, make a print with this negative and compare it to previous prints you have made with the same negative. By using this technique, you can quickly identify poor paper, and also chemicals, before you have expended considerable time and money.

SIZING OF THE PAPER

The image should sit on the surface of the paper rather than become embedded in its fibers. In addition, if the paper is too porous, considerable ferric oxalate-palladium salt solution will be needed to coat the paper adequately. To test the paper for porosity measure 50 drops or ferric oxalate solution (use Sensitizer A only; an excess is provided

with the kit) and try to coat an 8-by-10 sheet of paper as described later in these instructions. If you can completely coat the paper, then the porosity is not excessive: If you find you need more

than 50 drops, then-you will have to either size your paper or switch to another type or brand of paper.

Uniform sizing fills the pores of the paper with starch and provides surface for the image. Sizing was imperative the early days of palladium printing because of poor paper quality. Today sizing may or may not be needed depending upon the quality of the paper you choose.

Preparation of Sizing Solution: Your kit contains 20 g of arrowroot starch. Place this starch in a 1-liter container that you can heat (such as a saucepan) and add a small amount of hot water, about 20 ml. Stir the mixture into a thick cream. Be sure that no lumps remain. Add 1 liter of hot water with constant stirring. Boil the mixture for 5 minutes, then let it cool to room temperature. Skim off any scum or decant the clear solution into a storage container.

Application of the sizing Solution: Pin the paper to a board and apply the sizing solution to the surface with a clean brush. Brush the solution onto the paper, first across, then up and down, until the paper is completely wet. Using another brush like a clean shaving cream brush, to work the surface until it loses its gloss. Allow the paper to dry, either hung or still pinned to the board.

FOR YOUR CHEMICAL SAFETY

All chemicals are dangerous and must be treated with respect. The palladium printing kit contains a chemical that needs special attention: Potassium Oxalate.

Potassium Oxalate: This compound is an anticoagulant (prevents blood clotting) and a poison. Since this chemical is used as a developer, it can easily come into contact with your skin. It is strongly advised that you use tongs to develop palladium prints or wear rubber gloves if you feel you need to handle the prints during development. Should potassium oxalate solution come into contact with your skin, wash immediately with soap and water.

Other chemicals in the Palladium Printing Kit: You should be aware of the potential hazard of two other chemicals in the kit. Ferric Oxalate, like potassium oxalate, is a poison. You will be using only very small amounts of this chemical. Should you spill it on your skin, wash with soap and water. Potassium Chlorate, a dangerous and explosive chemical, is also supplied in your kit. However, the amount is so minuscule that no special precautions need be taken. If you find it necessary to dispose of solid potassium chlorate, flush it down a drain with lots of water. Do not dispose of solid potassium chlorate in a wastepaper basket of garbage can. It is an oxidizer and, under the proper circumstances, can supply oxygen to a fire.

The user assumes all risks upon accepting these chemicals. IF FOR ANY REASON YOU DO NOT WISH TO ASSUME ALL RISRS, PLEASE RETURN THE CHEMICALS WITHIN 30 DAYS FOR A COMPLETE REFUND. **Consult with local sewer and water authorities regarding proper disposal of darkroom chemicals in your area**

FERRIC OXALATE

The photographic term "ferric oxalate" is a misnomer, which has given rise to a considerable amount of confusion in the photographic literature. There are two common forms of this compound; tripotassium ferric oxalate (K3 Fe (C2 04) 3) and trihydrogen ferric oxalate [$H_3Fe(C_20_4)_3$]. While both forms are photosensitive, only the acidic form is sufficiently photosensitive to be useful in photography

The original formulas for palladium printing call for dissolving solid ferric oxalate with an excess of oxalic acid. With the original directions, it is not clear which of the two forms of ferric oxalate are to be used. Solid tripotassium ferric oxalate is a trihydrate that is thermally stable up to 110° C and stable in the dark for extended periods of time. The solid can be used in subdued room light; however, the solid is destroyed, turns from green to brown, when exposed to ultraviolet light.

Tripotassium ferric oxalate is photoactivated by placing it in an acid solution, where it is converted to the trihydrogen form. Photographers' Formulary Does Not recommend the use of the green, solid tripotassium ferric oxalate for platinum, palladium, or kallitype printing. Its photoactivity is low and it is difficult to convert to the more active form.

The ferric oxalate supplied with your kit is a 20% solution of trihydrogen ferric oxalate. This chemical is prepared by Photographers Formulary by the iron alum-oxalic acid procedure and contains a slight excess of oxalic acid. This ferric oxalate is ready for use as Sensitizer A without additional mixing. Sensitizer B does require additional mixing; see below.

Trihydrogen ferric oxalate is photosensitive to light in the 460-nm region. As a photosensitive material, ferric oxalate is very slow when compared with silver grain-emulsions. However, ferric oxalate should still be used in a darkroom with red safety light. Trihydrogen ferric oxalate is probably heat-sensitive, but the exact extent is not known. To be on the safe side, do not heat the solution, or the sensitized paper when it is being dried, over 50°C/120°F. Trihydrogen ferric oxalate is very water-soluble and its solution has a yellow to yellow-green appearance when first taken into room light.

Chemical Test for Photoactivity and Excess Ferrous Ions in Ferric Oxalate: In a suitable glass container (a test tube or a whiskey shot glass), place about 2 crystals of potassium ferricyanide (Catalog no 10-1010) and about 2 ml of water. Stir until the solid has dissolved. In the darkroom under a red safety light, add 1 drop of ferric oxalate. Hold the test container up to the red light in such a way that you can see through it as you add the drop of ferric oxalate.

If the ferric oxalate does not contain excess ferrous ions, you will observe only a slight darkening of the solution. If excess ferrous ions are present, the test mixture will turn very dark or black (It actually turns blue). Step out of the darkroom and quickly look at the test container. The solution should appear yellowish brown to orange. If traces of ferrous ions are present, it will appear green. It may have a blue cast. The deeper the blue, the poorer the quality of the ferric oxalate.

Hold the test container up to the side of a 100-watt frosted light bulb. Within a minute you should see a deep blue coloration forming on the side of the test container nearest to the light bulb. The formation of the deep blue color indicates that there is photosensitive ferric oxalate present. This blue is due to Prussian blue, which is formed by a reaction between the newly formed ferrous ions and the ferricyanide ion.

With a little practice using exposed and unexposed solutions of ferric oxalate, you will be able to gauge the quality of the ferric oxalate before you mix it with expensive metal salts.

PALLADIUM SALTS

Your kit contains either 15 ml or 30 ml of 15% palladium salt solution prepared from Sodium Tetrachloropalladate (Na2PdC14).

MIXING THE SOLUTIONS NEEDED FOR PALLADIUM PRINTING

Three solutions need to be mixed before printing: Sensitizer B, Citric Acid Solution, and potassium oxalate developer. Sensitizer A and the palladium salt solution do not need additional mixing.

SENSITIZER B. The kit contains two bottles of 30 ml ferric oxalate solution. One of these bottles is to be used as Sensitizer A and the other is to be converted to Sensitizer B. Your kit will also contain a packet containing 0.26 g of potassium chlorate. In a darkroom, add the contents of the potassium chlorate package to one of the ferric oxalate solutions. There is only a very small amount of potassium chlorate in the package, therefore, be sure that all of it is transferred to the ferric oxalate solution. Cap and shake the' bottle to dissolve all of the solid chlorate.

In the photo process, when ferric oxalate is struck by light, ferric ions are reduced to ferrous ions, which subsequently convert the palladium salt to free metal. The purpose of the potassium chlorate is to reconvert the ferrous ions back to the ferric state. Thus the chlorate acts as a restrainer, increases contrast, and maintains the whites.

The chlorate in Sensitizer B will slowly decompose over a period of weeks and the solution will lose its potency. It is wise to run a test strip about once a week or just before a printing session.

DILUTE CITRIC ACID: Place 1000 ml of water at 120°F in a storage container with a plastic cap and add 30 grams of citric acid. Stir the solution (or cap and shake the container) until the citric acid has dissolved. When dissolved add 1000 ml of cold water to bring the final solution to 2000 ml.

This dilute citric acid is much weaker than that used to clear platinum prints. Palladium metal can be etched from a print by a more concentrated solution of acid.

POTASSIUM OXALATE DEVELOPER: Your kit contains 227 g of solid potassium oxalate. Place the solid in a storage container, add 700 ml of water, and stir the solution. Not all of the solid will dissolve. This saturated potassium oxalate solution is the developer. It has an indefinite life and may be replenished with fresh solution to maintain volume.

SENSITIZING THE PAPER

AREA COVERED
Assuming 20 drops per ml, the 15-ml 20% palladium solution should contain sufficient solution to cover 12.5 sheets of 8 X 10 paper (50 sheets of 4X5). The 30-ml of Palladium solution should cover twice as much. In practice you will find that 15 ml will cover about ten 8 x 10's.

MIXING THE SENSITIZER: To sensitize the paper, a mixture of Sensitizer A, Sensitizer B, and palladium salt is prepared in the darkroom. The paper is coated with the mixture, then dried. Print contrast is controlled by the amount of Sensitizer B that is added to the mixture.

To mix the sensitizer mixture, use one of the following formulas:

SOLUTION	PARTS	DROPS FOR A 4x5 PRINT	DROPS FOR AN 8x10 PRINT
FOR VERY SOFT NEGATIVES;			
Solution A	0	0 drops	0 drops
Solution B	0.478	6 drops	22 drops
Palladium Solution	0.521	6 drops	24 drops
FOR SOFT NEGATIVES (HIGHLIGHT DENSITIES ABOUT 1.1)			
Solution A	0.174	2 drops	8 drops
Solution B	0.304	4 drops	14 drops
Palladium Solution	0.522	6 drops	24 drops
FOR AVERAGE NEGATIVES (HIGHLIGHT DENSITIES ABOUT 1.3)			
Solution A	0.304	4 drops	14 drops
Solution B	0.174	2drops	8 drops
Palladium Solution	0.521	6 drops	24 drops
FOR MODERATELY CONTRASTY NEGATIVES			
Solution A	0.391	5 drops	18 drops
Solution B	0.086	1 drops	4 drops
Palladium Solution	0.521	6 drops	24 drops
FOR VERY CONTRASTY NEGATIVES (WITH NORMAL SHADOW DETAIL AND HIGHLIGHT DENSITIES ABOUT 1.5)			
Solution A	0.478	6 drops	22 drops
Solution B	0.0	0 drops	0 drops
Palladium Solution	0.521	6 drops	24 drops

TO PREPARE A DIFFERENT VOLUME OF SENSITIZER MIXTURE

To prepare a volume of sensitizer solution other than that given for a 4X5 or an 8X10 print size, use the ratios given with each group.

Example: Suppose you determine that you need 55 drops of the mixture to cover an 8X10 sheet of paper, and your negative is average.

Calculations:

1. Multiply the ratio given by the total volume needed (55 drops in this example).

VOLUME

	ratio	times	volume needed	equals
Solution A	0.304	X	55 drops	= 1.67 drops
Solution B	0.174	X	55 drops	= 9.6 drops
Palladium Solution	0.521	X	55 drops	= 28.6 drops

2. Round the calculated number of drops to the whole numbers. Since you cannot measure a fraction of a drop, you will have to use a 56- drop mixture; Solution A, 17 drops; Solution B, 10 drops; and Palladium Solution, 29 drops.

SENSITIZING THE PAPER

Cut your paper at least 2 inches larger in both length and width than the negative size you will be printing.

Before sensitizing the individual sheet, inspect the paper via transmitted light to see if there are any large specks of impurities in their fibers. Use the cleanest piece of paper you have. Do not touch the surface of the paper with your fingers or any other material. Secure your paper to a sheet of glass (or plexiglass) by all four corners with masking tape. Pencil in the area to be covered with the sensitizer solution. Simply tracing around the negative sleeve containing the negative will suffice for this purpose.

Always wear protective gloves and an apron while coating your paper. Fill a clean glass with distilled water and rinse out the coating brush. Squeeze out all the excess water from the brush; it should be only damp, not wet. Select the sensitizer formula appropriate for the negative to be printed. Measure out the drops of A, B and C solutions in a small glass and gently swirl the glass to mix the solutions together.
Pour the sensitizer into the center of your paper and immediately, but with gentle pressure, brush the sensitizer over the area of your paper. Brush in only one direction. Allow the sensitizer to soak into your paper for at least two minutes, while the paper is still taped to the glass.

DRYING THE PAPER

Hang the paper up in your darkroom and allow it to air-dry for another 8-10 minutes. While the paper is drying, rinse out your brush and sensitizer glass with distilled water. Repeat this procedure after each paper coating. After the paper has air-dried for 10 minutes, blow-dry the front and back of the paper with your hairdryer set on warm not on hot. Keep the heat source at least 6 inches away from the paper during drying. Blow-dry each side of the paper for one to two minutes.

The drying procedure is important to the success of the finished print because the sensitizer must have sufficient time to soak into the paper, so that it will be held firmly in place during chemical processing. If insufficient drying occurs, the sensitizer will remain on the surface of the paper and two results will occur:

1. The finished print will lack the desired contrast, due to the paper being damp during the exposure.

2. Some of the palladium metal will float off the paper during processing, which will also weaken the intensity and tonal range of the finished product.

If too long a drying time is allowed, the sensitizer will sink too far into the paper fiber and the finished print will appear flat because the paper texture will scatter too much of the light reflecting from the paper surface. In addition, too much heat may decompose the sensitizer, which will, in turn, cause uneven tonal densities in the finished print.

EXPOSURE

Ferric oxalate absorbs in the ultraviolet region of the spectrum. Therefore you will have to use sunlight. (An enlarger will not work). You may also use an ultraviolet light source. It is difficult to obtain consistent results with sunlight. Ferric Oxalate is extremely slow. Exposure will take 10-2O minutes. It is advisable to run a test strip to calibrate your equipment setup.

HOW THE CONTACT PRINTING FRAME WORKS

The Platinotype Process is a contact printing process, which requires the use of a hinged-back contact printing frame to keep the negative in tight contact with the sensitized paper during exposure. This tight contact is necessary to guarantee sharpness and details in the finished print. Photographers Formulary manufactures just such a print frame in 8X10, 11X14, 16X2O, and 20X24, catalog nos. 07-2000, 07-2005, 07-2010 and 07-2020 respectively.

After sensitizing and drying the paper, disassemble the printing frame and clean both sides of the glass. Use dust-off to clean the negative. Place the sensitized paper, face-up, on the felt side at the hinged-back of the frame. On top of the sensitized paper, place a clean sheet of clear acetate - ideally no more than .003 to .005 mm thick. (This material can be purchased at an art supply store.) Place the negative, emulsion side down on top of the clear acetate, and finally place the sheet of glass on top of the negative. This whole section is then returned to the frame and held in place by the metal pressure clips.

The use of clear acetate is not a necessity, but will serve to protect any valuable negative from possible chemical staining due to being printed in contact with a damp piece of sensitized paper.

Place the assembled print frame, containing the paper and negative under the exposing light source. If a sunlamp is used, keep the bulb at least 2O inches above the frame during exposure. Make notation of the time at the beginning of the exposure, and note the duration of the exposure time for future reference when printing a particular negative. After the exposing the print, remove the paper and negative from the contact printing frame and process the print as described in the following section.

PROCESSING THE EXPOSED PRINT

DEVELOPMENT: Immediately after exposing your print, place some of the saturated potassium oxalate solution in a tray, which may be room temperature or 90/100F degrees F. Always use plastic or wooden tongs to handle the print during processing. Development will occur almost immediately especially if you heat your developer, which will allow for shorter exposure time for the provisional image.

One word of caution when working with a heated developer solution- because development occurs almost immediately it is important to submerge the print quickly and evenly into the developer solution to avoid streaking and uneven development. Also watch for air bubbles that may form on the surface of the print. If this should occur, brush over the area immediately with a soft hairbrush. Whether using the developer at roam temperature or heated allow the print to remain in the developer solution for at least two minutes. You cannot overdevelop a Palladium print.

ETCHING

After development, remove the print from the tray and allow the excess developer to drain back into the tray. Then transfer the print to the first of three trays of dilute citric acid. Allow the print to etch in the first bath for five minutes with intermittent agitation. After five minutes remove and allow to drain. Place it in the second acid-bath and repeat the procedure. After five minutes, remove and place the print in the final acid bath for five minutes. The acid in the first tray will soon become cloudy and yellowed in appearance. This is due to any remaining ferric oxalate being etched from the paper. When this occurs, discard the solution in the first bath, and move the second and third trays into the first and second positions and fill the third tray with a fresh acid-bath. The third tray should always contain a clear acid solution.

A word or caution about etching the developed print. This is a critically important part of the process, and is usually passed over too casually. However, if the print is not properly etched, it will darken with age and in this way can be destroyed. It is also important not to forget a print in any of the acid-baths. Air bubbles may form on the surface if the print is left to float unattended, and will cause uneven etching of the ferric oxalate in the paper.

WASHING THE FINISHED PALLADIUM PRINT

After development and etching, the palladium print must be washed thoroughly to remove as many acidic residues and heavy metal impurities as possible. The recommended washing rate is a complete exchange of water every 5 minutes for an hour: This can be accomplished by either discarding and refilling the water bath every five minutes twelve consecutive times or by allowing the water to flow through the bath, so that the water bath is fully refreshed every five minutes. The water should be no colder than 68°F/20°C and we highly recommend the use of distilled water.

After thoroughly washing, the print is hung up and allowed to air dry. With most papers the print will return to an almost flat condition after drying. If the print should curl it can be gently pressed flat in a dry-mount press set at 150°F.

PHOTOGRAPHERS'
FORMULARY INC.

PO Box 950 • Condon MT 59826 • 406-754-2891 • FAX 406-754-2896
E-MAIL formulary @montana.com