Chapter 1 - Introduction

Chapter 1 - Introduction
Brief History

The platinum process descended from other iron based processes such as Cyanotype in the mid 1860's. Known as Platinotype, it was patented by William Willis, of Great Britain, in 1873. The Platinotype gained much popularity being both beautiful and the most archival of any printing process. With the increasing cost of platinum and the mass production of fine gelatin silver papers in the mid 1930's, Platinotype fell by the wayside. Although, several photographers continued to make fine platinum prints.

In the early 1970's two things happened. Commercial gelatin silver paper was lessening in quality. And, George Tice wrote an article on hand coated platinum prints in *Caring for Photographs*, a volume of the Life Library of Photography published by Time Life Books in 1972. This rekindled the interest in hand coated platinum prints. Several contemporary photographers prefer to utilize this process because they find the platinum print to be a most beautiful object. Many find that the Platinotype process more closely represents the way they wish to see the image.

For some fascinating information on the history of the platinotype, read *The Eighth Metal: the Rise of the Platinotype Process* by Mike Ware located on his web site. Early references to the Platinotype Process can be found in the various editions of the *Silver Sunbeam*.

Description

The platinum-palladium (Pt/Pd) process is an iron based process. Other, different iron based processes include Cyanotype and Kallitype. The light sensitive component of the platinum-palladium process is Ferric Oxalate. Upon exposure to light the Ferric Oxalate is transformed into Ferrous Oxalate. The basic difference is that Ferric has a covalence of +3 and Ferrous has a covalence of +2. These are differences in the associated electrons which cause the molecule to bond differently. A property of the Ferrous Oxalate is to reduce Noble metals from their double salts and revert back to Ferric Oxalate. This reaction is known as Brewster's Reaction. Platinum and Palladium are Noble metals. The resulting print consists of these pure Noble metals imbedded in the fibers of a substrate.

The Ferric Oxalate sensitizer provides for what is termed a Develop Out Process (DOP). The image prints out partially and must be enhanced by use of a developer (although this not actually a developer or a development, but rather an enhancement.) Another sensitizer, Ammonium Ferric Oxalate, provides in certain occurrences for what is called a true Printing Out Process (POP). The image prints out fully with exposure. No development or enhancement is necessary. Both of these sensitizers are used to make Pt/Pd prints and provide for differing results in the prints.

The sensitizer is most sensitive to the Ultra Violet (UV) and blue portion of the light spectrum. However, it must be remembered that the Ferric Oxalate will also react to heat and time. It is a good technique to expose within an hour of coating DOP and immediately upon coating and drying POP. An unexposed coating is susceptible to change and deterioration even if hermetically sealed and frozen.

The platinum and palladium salts may be used interchangeably or in combination, with each scenario producing unique qualities in the photographic print. The metals can be mixed into an aqueous solution useful for this process when they are in the form of a double salt. The double sat is basically the Nobel metal chloride (such as $PdCl_2$) combined with a chloride salt (such as NaCl). The platinum double salt is typically that using Potassium, K_2PtCl_4. However the ammonium salt $[(NH_4)_2PtCl_4]$ is sometimes used. The palladium double salt can be any of the period I chloride salts or ammonium. It is important that the salt and double salt be soluble in water.

Note: At this point, the author is currently using K_2PtCl_4, Li_2PdCl_4, Na_2PdCl_4, and K_2PdCl_4.

It is important that a sufficient amount of metal be deposited into the substrate that will provide optimum image quality. An amount of metal beyond that will only be wasted, while not enough metal will result in a weaker print. Each metal salt has an optimum solution for a particular sensitizer. The simplified chemical equations for the Pt/Pd process are presented in the section "Process Equations" in Chapter 6, Chemistry. Optimized formulas for the metallic salts are found in the next section of Chapter 6.

Contrast can be altered with several contrast agents, materials and techniques. It is highly suggested that near to correct contrast (if erring, on the low side) be given to the negative.

Everything other than pure metallic platinum and/or palladium is cleared from the print with a clearing solution. The final result is the platinum and/or palladium metals embedded in the fibers of the substrate.

Please note that all of the methods, procedures, techniques, items, and things within this guide have been tried and tested by the author. Those that work are currently in use by the author, and those that don't are so stated. Every paper, chemical, or process variation can produce a unique nuance in the print and an incredible amount of diversity and control. After gaining proficiency in this process, it is important that various new materials be tried.

Technique is the key to control. Technique is presented fairly well in this Guide, but it is something that has to be mastered. Only with much practice will experience develop. Experience will then provide insight into the materials, process, and technique. Experience becomes the key to connecting the print to the eye.

There are certainly many untried and undiscovered nuances of the Pt/Pd process. Additions or modifications may be made to this guide at any time. Any questions or comments can be served via E-mail.

Tips

Some general recommendations follow.

★ It is recommended that this process be learned using 4x5 negatives. In this way it should cost less to master the process, and the prints should still be of a large enough size to evaluate. The 4x5 size negative is also the easiest to individually process.

★ Go easy with filters on the camera. This process can discriminate extremely subtle differences in tonality. What may call for a #8 filter in silver printing may only require a #3 filter in this process. (Note: If heavily filtered dark skies are what's wanted, print them in gelatin silver. The results will be much better. One should always take advantage of the particular nuances any process or material has to offer.)

★ The negative should be made in agreement with the process as well as the subject. The platinum palladium process utilizes more of the negative's information demanding a more carefully controlled negative. It is a advisable that one complete the Matrix described in the Negative Control section. With this process there is little room for exposure or development error if the highest quality and full advantage of the unique attributes are expected.

★ The amount of UV light required to print a platinum-palladium photograph dictates that the most efficient method of exposure be contact printing. An enlarger lamp would likely cause damage to the negative before enough light could expose the print or take an extremely long time. Enlarged prints can be made however, by building larger negatives. In order to get the proper densities in these negatives (which also require masking), a good understanding of the platinum-palladium process is required. It is recommended that one first master negative control and printing before attempting negative building.

★ The sooner one moves away from using kits, the better. Better still, DON'T USE KITS. Kits or pre coated material deprives one of some of the essential elements and understanding of platinum-palladium printmaking.

★ Some kit materials can be put into use or modified so as to not go to waste. See the section Modifying an Existing Solution in Chapter 6.

★ The intent of this guide is that when starting out, one could do exactly and only exactly as in this guide and learn to make quality Pt/Pd prints. It is recommended to not change anything until that which is specified is mastered. A check to see if one is ready to modify or deviate is that they have mastered enough to throw away this Guide and write their own.

★ Always remember, if one does not get CONSISTENT results, then THEY must be doing something incorrect. With the proper control, this process is very consistent.

Workroom Considerations

Lighting
Electrical
Plumbing
Sink
Ventilation
Ambient Control
- Heating
- Cooling
- Dehumidifying
- Humidifying

The Platinum Palladium process should be performed in a work space capable of providing for safety, control, and consistency. It is suggested to first lay out and draw the entire work space on paper carefully considering all components and the flow of the work. If more than one person is to be in the workroom, ample space should be provided for an uninterrupted work flow. It is most convenient to be able to construct the entire workspace, including walls, but in many situations the work space must be designed to fit within an existing space. The design characteristics should include those of a standard film processing area and include the following.

Lighting - The area must be light tight but have ample light for working. All areas should have switchable bright white illumination and appropriate safelights for film used and Pt/Pd materials. Although not as sensitive as film, Pt/Pd coatings can be fogged by stray light. See the section on Safe light for the appropriate lamp to use for Pd/Pt. The Pt/Pd safelight(s) should fully illuminate all work areas.

Electrical - All outlets should be GFI (Ground Fault Interrupt) protected. Each work surface or area should have at least four outlets, including the sink area. Outlets should be placed above the work surfaces such as with kitchen counters. Outlets at a sink should be high enough to avoid being splashed upon. Two or three 20 Amp circuits should be used for the outlets. An additional two or three 20 Amp circuits should be used for ambient controls and ventilation. One 15 Amp circuit should be used for lighting. All electrical should adhere to all codes.

Plumbing - It is recommended that water be filtered to 0.5 microns. It is convenient to have both hot and cold water and a mixing valve. The entire drain and source lines near the sink should be plastic (PVC, CPVC). It is suggested to have several valves along the sink to which tubing can be attached. Any metal in the vicinity of the sink will likely corrode (including valves). A large plastic bucket is a must for proper dilution and disposal of spent developer, clearing baths, and other solutions suitable for drain disposal after neutralization and dilution. Solvents should not be needed, but if ever used should be recycled and NEVER disposed of down the drain. All acids and other suitable solutions are neutralized in the bucket, diluted, then disposed of down the drain. Drain pipes should be plastic and not iron. All plumbing should adhere to all codes.

Sink - Two sinks would be ideal as Pt/Pd and film processes do not agree. 3 x 10 feet minimum should be the sink size considered for up to 16x20 inch prints. If only one sink is used, it should be thoroughly washed when changing from film to Pt/Pd. The sink can be made of wood with an epoxy paint. Plastic grids, as those used with fluorescent lamp housings, can be placed on wood bars above the sink bottom to keep the trays elevated. Stainless steel and other metals should not be used and will have Pt and Pd transfer to it and may be etched by the acids and solutions used.

Ventilation - Air must enter the room as well as leave the room. The best exit location is along the entire back of the sink. In this way, fumes from processing, as processing is done in the sink, will be removed by the shortest path. The input location should be the farthest from the sink and on the other side of coating and exposure areas. Any dust from coating and ozone from lamps should readily enter the path of the air flow. This will direct the design and layout of the room. A heat exchanger built into the ventilation system can dramatically save on heating and cooling costs. Any air entering the room should be filtered. The air path in a properly designed system should enter through a filter; pass through a heat exchanger; be ducted to the farthest point from the sink; be cooled, heated, humidified, or dehumidified; pass through the coating area; pass through the exposure area; pass over the sink; enter ducting along the back of the sink; pass through the heat exchanger; be ducted to the outside away from the intake. The appropriate ducts should be insulated. It is useful to have variable speed control as the airflow can be slower when it is not necessary to evacuate a lot of fumes. This will help with control of the ambient conditions. When needed, the ventilation flow can be increased. The maximum airflow should be that necessary to keep the air quality at a safe and comfortable condition. A good design of laminar flow across the sink area should allow for lower air flows.

Ambient Control - Ambient control is a serious consideration with the Pt/Pd process. There are certain conditions which have dramatic affects on the print. Consistency and control can be regulated with the ambient conditions.

Heating - Heating is primarily for the comfort of the individual. A small ceramic space heater can easily supplement what is lost by the heat exchanger. The temperature should be typically less than 70°F.

Cooling - High temperatures can play havoc with this process. When using the Ammonium Ferric Oxalate sensitizer (POP), it is recommended to keep the ambient temperature below 70°F. As the temperature increases above 70°F, grain in the print increases. At above 90°F, this graininess is so profound that the image blurs and becomes splotchy degrading more at higher temperature. The ambient temperature should be kept below 70°F with Ferric Oxalate (DOP) as well. A air conditioner should be located as per the ventilation design. An air conditioner is also important as the

dehumidifier can produce a good amount of heat while running.

Dehumidifying - DOP works better at lower relative humidity (RH), the lower the better. One cannot get the paper "bone dry" at high levels (>50%) of RH. This most likely results in a lack of maximum density. For DOP it is suggested to keep the RH below 40%. With POP, the highest recommended RH is 70%. At higher RH the probability of producing a quality print diminishes quickly. In some climates, if one dehumidifier doesn't do the job, try two. Remember that the outside humidity is coming in with the ventilation.

Humidifying - With POP, the higher the RH, the cooler the color of the image. The best way to humidify is with a sonic mister. This can be the same mister used for humidifying the paper prior to coating. A more constant ambient RH may be achieved by running the dehumidifier and mister at the same time.

An Outline for Learning the Pt/Pd Process

The intent of this section is to provide orderly guidance for learning the Pt/Pd process. As prerequisite, it is assumed that the novice has experience and a full understanding of operating a camera, processing film, the Zone System, and general photography. The Pt/Pd process requires some basic skills in chemistry and photography and utilizes some expensive materials. There are many less time consuming and less expensive photographic processes one can pursue. One should not consider the Pt/Pd process without having the dedication and commitment it demands. If one wishes to try their hand at this process, it is recommended that they attend a workshop or obtain personal instruction from an experienced Pt/Pd printer. Only after a firm commitment is decided on should they purchase all the materials necessary. It is recommended that one NOT work from kits, pre-coated material, or other shortcuts as this will not provide the level of quality results nor the necessary experience.

The follow steps roughly outline a recommended sequence referenced to the various sections throughout this guide. It should be expected that one technique or activity may be dependent on others. One should not become surprised if after learning a particular technique, they find that they must modify it after learning something else. The information in this guide has been assembled over years and decades. As new discoveries are made, sometimes old procedures or techniques must be modified. A key to developing good technique and procedure is achieving consistency of results. Much of the effort into what may seem tedious study or careful control circumvents the many potential pitfalls and problems one is likely to encounter.

Throughout this guide a distinction has been made of several terms.

Process - is the set of procedures which utilizes certain materials under certain conditions and employs certain techniques to produce a certain result (such as the Pt/Pd process). One selects the process, but does not alter the process. Once a process is fully understood, one may develop sub-processes or variations of the process (such as DOP [Develop Out Process] and POP [Print Out Process]).

Procedure - relates to the steps or group of steps of a process. Procedure may be influenced by variations in conditions or technique, but procedure is independent of personal technique. One generally sticks with a procedure that works and only modifies it when study shows a necessity. Technique is modified to accommodate procedure.

Technique - relates to events dependent on the individual and their personal skills. One's technique may differ from another, but the final result should be the same. For example when weighing, the same weight should be concluded from whatever personal technique and equipment is used. One must determine and master their own techniques. Techniques may be borrowed and practiced, but are typically modified to personal desire. It is important that one carefully develop their techniques so as

to be conducive with the greatest success. Consistency and accuracy are important qualities of technique.

Method - relates to a sub-procedure or set of procedure which can lead to similar process or sub-process results (examples are: single or multiple coating methods; digital or analog negative methods). One can choose from several known methods or develop their own. However like procedure, the development of methods requires a good understanding of the process.

Conditions - are those such as temperature, relative humidity, pressure, environment and such and can be placed into two categories.

Boundary conditions are limitations that the process should or must operate within. For example: a safe light must be used to prevent exposure of sensitized material to the threshold of illumination that can convert the sensitizer.

Ambient conditions are those present which may cause variation of the results and should be monitored and controlled if necessary. For example: the relative humidity may be varied within a range (of boundary conditions) to influence color or other characteristics of the POP variety print.

The novice should be concerned with carefully following set procedures and methods, controlling conditions as required, and learning, developing and practicing their technique. It is recommended that the novice avoid attempting new variations and any modification of procedures or methods. After they fully understand and have mastered the techniques and the procedures of the Pt/Pd process, they are no longer a novice.

Steps are to be followed in the order presented.

Basic Information
Ready Equipment and Work Room
Ready Materials
Ready Stock Solutions
Study Coating
Learn the Process
Learn to Make Negative and Print
Photograph and Print
Further Study

Basic Information

To begin, one should first read Chapters 1 and 2.

Links to more info:

Chapter 1
Chapter 2

Now is the time to make the decision and commitment whether to pursue learning the Pt/Pd process. The cost of acquiring the necessary equipment and materials can be significant. Again, if one wishes to sample the process, it is recommended that they attend a workshop or obtain personal instruction from an experienced Pt/Pd printer.

While any size negative may be printed by the Pt/Pd process, it is recommended that 4x5 be used when learning. This size is large enough to control and analyze well and small enough to save on chemistry. If one does use smaller negatives, they must keep in mind that coating efficiency and coverage and the coating itself can be more difficult. The use of a smaller brush for small coatings will help. If one only has larger negatives, they should consider learning and practicing with a 4x5 portion of that negative.

Ready Equipment and Work Room

Read Chapter 4.
Purchase any equipment and make any modifications to the workroom that may be necessary.

Links to more info:

Chapter 4
Workroom Considerations
Vendors

Start with the equipment suggested throughout Chapter 4. As personal technique is developed some equipment may be changed or added. If one plans to use the sun as a light source, the artificial light source need not be built. One should take the time to properly set up and equip their work space for the Pt/Pd process. Remember to avoid cross contamination, have proper ventilation and lighting, have proper chemical storage, adequate ambient control, and enough space to work comfortably (including a coating area).

Ready Materials

Read Chapter 5 (except Preparing FO Powder, this is advanced work).
Purchase any chemicals and paper necessary.

Links to more info:

Chapter 5
Chemicals
Substrates
Vendors
Additional Information
on metal salts
on contrast agents

The following are suggested minimum starting materials and amounts:

distilled water [2 gallons]
Ferric Oxalate powder [25 grams]
Oxalic Acid [1 gram]
EDTA (60-00-4) [1 gram]
K_2PtCl_4 (platinum double salt) [5 grams]
PdCl2 (palladium salt) [10 grams]

NaCl, KCl, or LiCl (any one or all) [10 grams each]
contrast agent (any one, see info) [1 gram] (optional)
Potassium Oxalate [500 grams]
Sprint Fixer Remover [1 quart] (for clearing bath)
H3PO4 (phosphoric acid, 85%, reagent grade) [1 litter] (optional clearing bath)
Bienfang 360 paper [several pads](or Crane's Cover-90)

The quantities given are a minimum. Buying in larger quantities can be more cost effective and is a good idea if one is committed to continuing use of the Pt/Pd process. The quality of the chemicals is important. All chemicals listed here should be of ACS reagent grade, typically available from any ISO-certified manufacturer (except for the precious metal salts). The metal salts should be purchased from a special manufacturer such as Engelhard Corporation. However, Engelhard has a minimum order necessitating the purchase of larger amounts. Smaller amounts may be available from several alternative photography suppliers, although the quality could be suspect.

Other papers may be used, although Bienfang 360 is a good paper to learn coating by brush and is readily available from most art supply stores. If a rod is used, Crane's Cover-90 will not have the wrinkle problem of Bienfang and is an excellent paper.

Ready Stock Solutions

Read Chapter 6.
Prepare stock solutions.

The weighing of materials for the sensitizer, metal salts, and optional contrast agent must be done accurately and consistently.
Weighing and measuring are the first techniques to master.

Link to more info:

Chapter 6

Study Coating

Read Chapter 7.
Using some water with food coloring added, practice some coating. Follow the sections on coverage and efficiency, but at this point only use the colored water. Do not use the actual chemistry at this point.
This is the beginning of learning brushing or spreading technique.

Links to more info:

Chapter 7
Coating Coverage
Coating Efficiency
Coating Paper

Learn the Process

Re-read Chapter 7.
Read Chapters 8, 9, and 14.
Mix a coating solution.
Coat a paper.
Expose using any negative (do not expect this to be a wonderful print).
Process.
Repeat until the basic process is understood (at this point concentrate on understanding the process, not making a wonderful print.)
Determine coating coverage and efficiency (this is important.)
Try some other negatives that may do better.
Coating technique and the procedure of the process should become familiar.
Now the novice is ready to begin.

Links to more info:

Chapter 7
Chapter 8
Chapter 9
Chapter 14

Learn to Make a Negative and Print

Read Chapter 3.
Do the exercise and study outlined in Chapter 3.

This will train the eye to read the negative and the print and relate them to each other and to the original scene. This will also provide the proper negative to use with the materials selected to make a Pt/Pd print suitable to one's preferences. This also provides experience with producing prints consistently.

Link to more info:

Chapter 3

Having a complete understanding of this exercise will provide a strong foundation for mastering the Pt/Pd process.

Photograph and Print

Photograph, process negatives for the Pt/Pd process, and print.
Don't change anything or do anything differently. Just photograph and print.
This is the time to perfect technique and begin mastering the process.
Remember, the only modifications to be made at this point are in perfecting technique.

Further Study

Got some good prints? Now is the time for Chapters 10 and 11.

Chapters 12 and 13 offer information on negative building. One should realize that they should have a good understanding and command of the Pt/Pd process before building negatives for this process.

The studies in Chapter 15 or their inspiration may lead to advanced work and discovery of new variations in the process or refinement of procedures.