

**SODIUM CHLOROPLATINATE AS A
CONTRAST AGENT IN PALLADIUM AND PLATINUM PRINTING**

APIS October 2000

Table of Contents

Page 3 Sodium Chloroplatinate $\text{Na}_2[\text{PtCl}_6]$ as a contrast agent in standard platinum, palladium and Ziatype printing and its historical and practical issues.

By Richard S. Sullivan

Page 7 Chemical Conjectures on Sodium chloroplatinate as a contrast agent in standard platinum-palladium printing.

By Howard Efner

Forward

The following is two papers delivered at APIS (Alternative International Photographic Symposium) held in October of 2000, at the Royal Photographic Society in Bath England.

Both papers are to be considered informal and preliminary. My thanks to Howard Efner for his analysis of the contrasting function of sodium chloroplatinate. This was lifted from an email message and was never intended as a rigorous formal paper and should not be judged as such. I think it important enough for those who can understand chemistry at this level to have Howard's musings on this topic.

SODIUM CHLOROPLATINATE¹ Na₂[PtCl₆] AS A CONTRAST AGENT IN STANDARD PLATINUM-PALLADIUM AND ZIATYPE PRINTING INCLUDING HISTORICAL AND PRACTICAL ISSUES.

By

Richard S. Sullivan
Santa Fe, New Mexico

Ever since the modern revival of platinum printing in the late 70's printers have been searching for a way to increase contrast without graining and mottling in the print. The common choice is potassium chlorate for the traditional developing out system and ammonium dichromate for Ziatype POP printing. Almost every modern printer has noticed that when more than modest amounts of these contrast agents are used, the print almost invariably suffers from grain, unevenness, and compression in the middle tones. The mantra of contrast in platinum printing has been "get it in the negative."

Not all of us are so lucky as to "get it in the negative" and we occasionally return with negatives that are too soft. At Bostick & Sullivan we have been running our Help Line for more than 20 years and by far the number one problem for platinum printers is getting contrast in the print without graininess.

Background

Recently I was rummaging around in the lab and found a 20 year-old bottle of sodium chloroplatinite tucked back in a cabinet -- a dead soldier from some early experiments. Secondly, I happened to be re-reading Abney and Clark and came across a very oblique reference to Na₂PtCl₆. The coincidence of the two events piqued my curiosity.

My first attempt was to use it as the platinum salt in the Extravagatype process, a glycerin development pure platinum process discussed in *The New Platinum Print* by Sullivan and Weese. My first attempt was unsuccessful and I only got a hint of an image. I reduced the amount of Na₂PtCl₆ (sodium chloroplatinite) to half the metal salt and used the traditional K₂PtCl₄ (potassium chloroplatinite) for the other half. The result of my printing experiment was that I got an extremely contrasty print, however the print did not suffer from the mottling and graininess that is normally associated with this much contrast boost. I went on from there to experiment further with Na₂PtCl₆ in both the traditional developing out palladium process, and the POP Ziatype process.

Conjectures

My son Kevin and I have done extensive testing and we have found that it does increase contrast and can push it way up the scale compared to ferric oxalate No 2 without graining and

¹ Also known as sodium hexachloroplatinate, sodium platinichloride, di-sodium hexachloroplatinate sodium chloroplatinate

mottling. (See Figs 1 and 2) It also does not produce in the print the semi-posterized look that people notice when you push contrast with the standard potassium chlorate or ammonium dichromate. We suspect that the advantages are derived from the fact that the sodium chloroplatinate is actually participating in the making of the image, whereas the pure oxidizer compounds like the dichromate and chlorates are largely acting as restrainers and really are only highlight enhancers.

Historical Note

Abney and Clark in *The Platinotype: It's Preparation and Manipulation* noted the fact that this compound could be used to increase contrast² in 1898. Here is the relevant section from Abney and Clark:

*But any oxidizing chemical in any proportion can be practically used for this purpose, provided they do not form chloro-platinate in the mixture, which, once formed, could not be evenly applied to the paper. **It is therefore generally accepted that chlorate of potash is the best oxidizing substance to use; it appears to be almost without effect on the solution, only acting when this is dry.** The explanation of this is that the first action of the chlorate of potash on the iron salt is the formation of ferric chlorate; the salt is, however, unstable, and gradually, during drying, hands over its oxygen to the potassium chloro-platinite. The action of chlorate of potash is, however, very energetic, and it must be added with great care and scrupulous exactitude. The presence of such a minute quantity as one-hundredth per cent is said to make itself evident.*

If the sodio-chloro-platinite be used instead of the potassium salt, in that case, sodium-chloro-platinate can be directly added instead of chlorate of potash.
(Emphasis added)

As you can see, though they do not exactly dismiss sodium chloroplatinate as a contrast ingredient, they relegate it to a niche and do that without any positive comments. It appears that the rejection is based on the fact that they were discussing platinum printing; that is pure platinum in which the potassium salt is used. The second quoted paragraph says essentially that if you are using sodium chloroplatinite [Na₂ PtCl₄] as your base instead of K₂PtCl₄ (modern standard potassium chloroplatinite), then you may use sodium chloroplatinate [Na₂PtCl₆] as a contrast ingredient. Abney and Clark do not comment any further on this compound. Reading between the lines, the inference is that if you are using a potassium salt of platinum, potassium chlorate will hand off its oxygen to the platinum compound. If you are using the sodium salt of platinum, use sodium chloroplatinate {Na₂PtCl₆} as your contrast ingredient.

Abney and Clark's offhanded dismissal of sodium chloroplatinite as a contrast enhancer due to the fact that they believe that it is incompatible with a potassium platinum compound is largely irrelevant as modern printers use an emulsion base made up mostly of sodium palladium. I question their supposition about the mixing of potassium and sodium compounds and have found that Na₂PtCl₆ works perfectly fine with the potassium platinum salt.

² Available in its entirety on the Bostick & Sullivan web site.

Traditional method

Traditionally potassium chlorate is used in a second solution of ferric oxalate. The No.1. Solution has no chlorate, the No 2. has typically .33 gm of potassium chlorate per 25 ml of solution. Contrast is obtained by varying the ration of No. 1 ferric oxalate to No. 2 ferric oxalate. The No. 3. solution is the Palladium solution. A typical ratio might be this: 12 drops of No. 1, 3 drops of No. 2, and 15 drops of No. 3. This would be a slightly modest boost in contrast. Any more No 2 than this in the ratio and the print quality will almost certainly suffer.

In the Ziatype process we use a 1% to 5% solution of ammonium dichromate and add it to the emulsion in drops. The Ziatype seems to be slightly more tolerant than the traditional developing out method in terms of how much contrast one can boost without any ill effect but the limit is there. Sodium chloroplatinate also works well in the Ziatype process.

Using sodium chloroplatinate

Sodium chloroplatinate is used by substituting it with a portion of the metal salt (No 3) in a similar manner to substituting a portion of the No 1 ferric oxalate with the contrasty No 2 ferric oxalate as is done in the traditional method. As with any contrast enhancement print times will go up as you increase the amount of Na₂PtCl₆. A 50:50 ratio seems to be the practical limit but I suspect that in some circumstances it may be exceeded.

Processes that it can be used in.

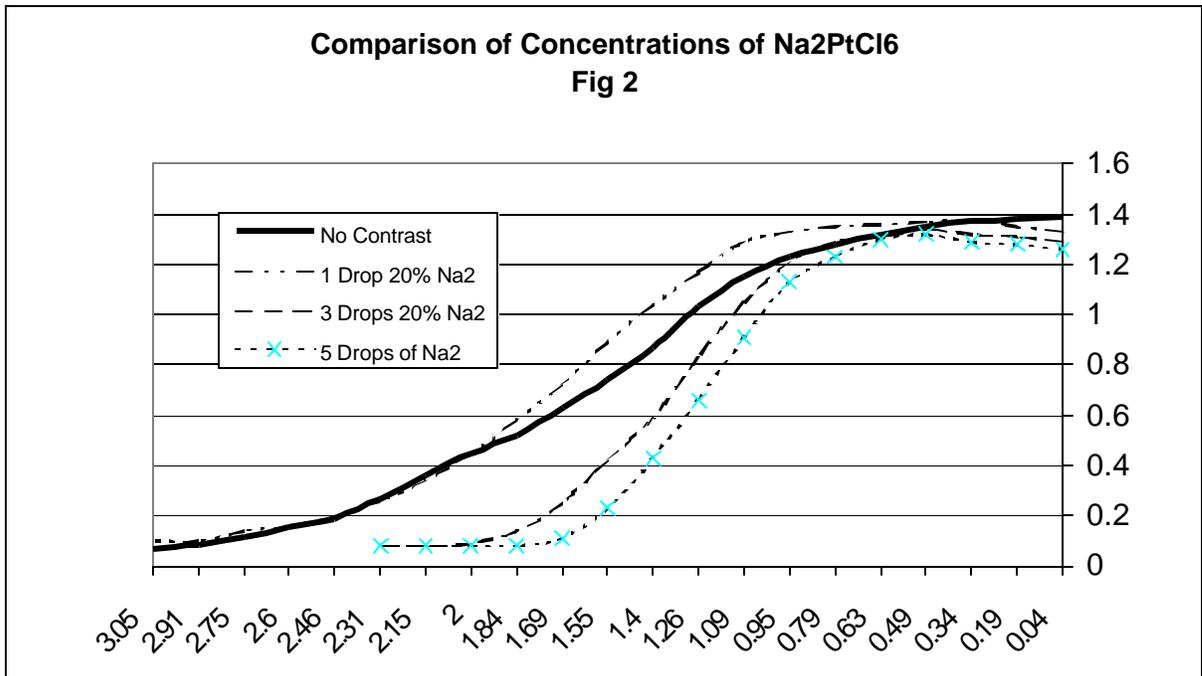
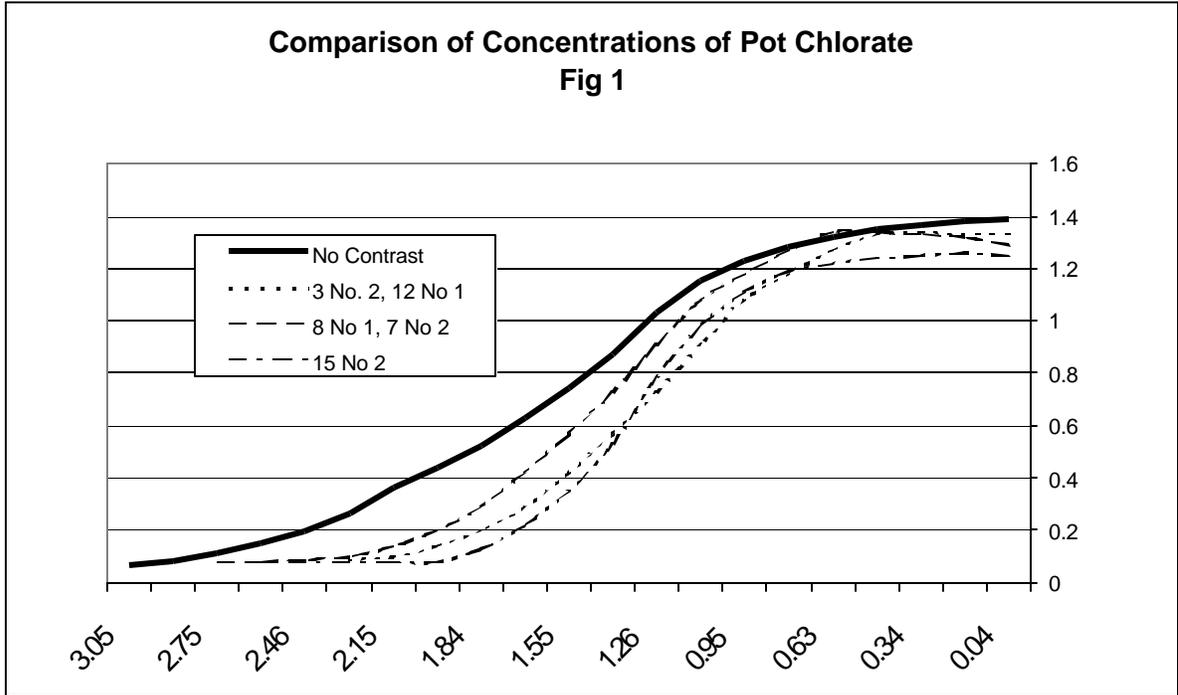
So far tests have shown that it can be used in the Ziatype (lithium palladium based POP), Standard Pt and/or Pd printing, Extravagatype (glycerinated developer with pure pt), and Pizzitype (potassium based platinum POP). When used in the Ziatype system there is a slight amount of clouding in the emulsion but this appears to be of no consequence.

Sodium tungstate

Sodium tungstate 40% solution is used in Ziatype printing as a colorant for achieving brown tones and as a contrast reducer. It works in standard palladium printing as well. I have only just done a little experimenting with sodium tungstate in conjunction with Na₂PtCl₆ and others may wish to follow up on this. I added 4 drops of 40% sodium tungstate to my Ziatype emulsion and then added 4 drops of 10% "Na₂" The tungsten lowered the contrast and the Na₂ raised it, but raised it more than the tungsten lowered the contrast. The result was a lusciously warm tone to the Ziatype, unlike the color one normally associates with sodium tungstate. Initial tests indicate that there may be a way to control both color and contrast independently with the skilled use of a combination of sodium tungstate and sodium chloroplatinate. This is an area for more experimentation. Remember to add the tungstate to the ferric oxalate solution before adding the palladium or platinum.

Fig 1 was made from emulsion sufficient for an 8x10 print. The metal salt comprised 15 drops of palladium standard No. 3 and the amounts of ferric oxalate No 1 and No 2 shown in the legend.

Fig 2 was also made from an emulsion sufficient for an 8x10 print. It was comprised of 15 drops ferric oxalate No 1 and 15 drops of total metal salt. The amount in the legend was the number of drops of sodium chloroplatinate 20% solution incorporated into the 15 drop total metal salt, the remainder being palladium Standard No 3.



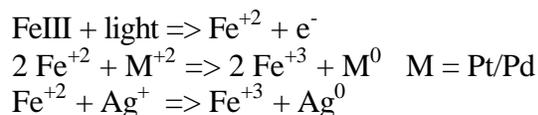
CHEMICAL CONJECTURES ON SODIUM CHLOROPLATINATE AS A CONTRAST AGENT IN STANDARD PLATINUM AND PALLADIUM PRINTING.

By

Howard Efner
Bartlesville, Oklahoma

Background

The details of the chemistry of iron printing processes are not well understood. While the basic reactions are quite simple, the details, such as image contrast, tone, and the role of the “inert paper support” are a swamp full of alligators.



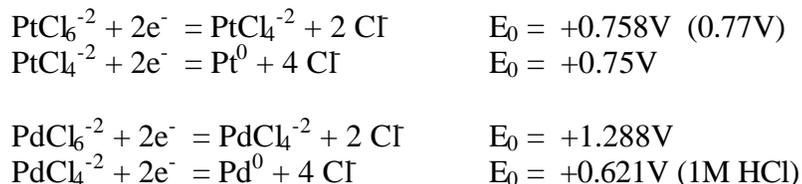
Not only are the thermodynamics of the reactions important to define the spontaneity of the reaction along with the extent of reaction at equilibrium, the kinetics (reaction rates) are important for things like image tone which is a function of particle size. Reaction kinetics call the shots when there are competing reactions. Simply put, thermodynamics tell you if you can get there, while kinetics tell you how long it will take.

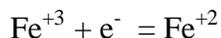
The electrochemical data, that is easily available, can give a rough idea of what may be occurring in the sensitizer layer of the print, but there will be a large margin of uncertainty. First, most of the published data is from carefully controlled laboratory measurements or estimated from other thermodynamic data (equilibrium constants or free energy data). These are all related as shown by this resurrection from P. Chem.:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = -RT\ln K = -nFE^0$$

The E_0 values in the literature are for the reaction at unit activity. The actual cell potentials are a function of, concentration, the ions present, and the solvent. In reality, the presence of oxalate, citrate, acetate, phosphate, etc will change the actual potential for a couple such as $\text{Fe}^{+3}:\text{Fe}^{+2}$. Some reactions, like ferrous/ferric are strongly influenced by the counter-ions that are present while others demonstrate smaller effects.

The following are some important electrochemical potentials for this chemistry:





$$E_0 = +0.77\text{V} \text{ (for aquo complex.)}$$

This voltage is very sensitive to the environment around the iron atom. The reported voltage varies from +1.14V for Iron(phenanthroline)₃, to +0.69V (acid) or +0.46V (basic) for Ferricyanide/ferrocyanide. In basic solution, ferrous hydroxide is reported to be a better reducing agent than ferrous ion.

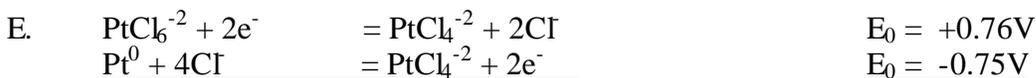
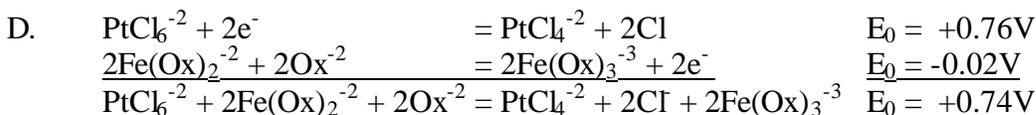
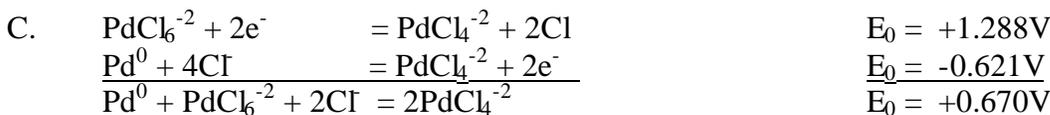
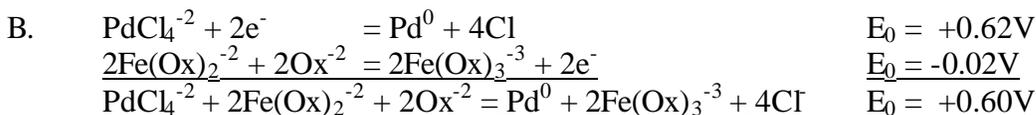
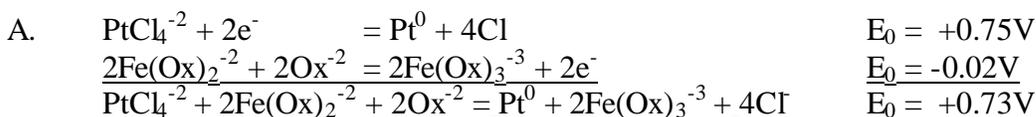
Found it in Latimer ("Oxidation Potentials", 2nd Ed, 1952, pg. 225)



This low potential for iron oxalates indicates that it is a fairly facile reduction of ferric to ferrous and can account for the photosensitivity of ferric oxalate. This also is a key to why trace amounts of contaminating reducing agents can cause your bottle of ferric oxalate to go bad with time. It also demonstrates that ferrous oxalate should be a good reducing agent. The potential is there, but it does not describe the kinetics.

Latimer also reports that both chlorate and perchlorate are strong oxidizing agents, based mainly on thermodynamic data, but exhibit unusually slow kinetics. Also, as the reactions of either perchlorate or chlorate start, the reduction products are more reactive than the starting materials so the whole system can accelerate (sometimes with explosive results). A hot solution of chlorate is reported to be reduced, fairly rapidly, by ferrous ion. The electrochemical half cell potentials for various chlorate reactions are numerous and very dependent of path. Enough said.

From the above data, the following reactions can be written.





For PtCl_6^{-2} attacking Pd^0 , the cell voltage would be about +0.14V, while the reduction by ferrous oxalate is +0.74V, and should be favored.

How Na2 may work

Now we all take a big leap of faith into the land of SWAG and hand waving. The following is speculation and theory. But what the hell, here goes.

One method to increase the contrast in a Pt/Pd image would be to rapidly attack the trace ferrous salts in the highlight regions and use them to reduce something to a non-image producing product. There would not be a high concentration of ferrous oxalate in these regions, so it would not take too much reagent to cause the change. As mentioned above, ferrous ion will reduce chlorate in warm solution with the reaction being a kinetically controlled process. While this chemistry is waiting to happen, the ferrous salts can be busy doing other things, like making grainy images while waiting for chlorate to diffuse and react. Chlorate is a reasonably good complexing ion so it probably exchanges with the chloride in the Pt and Pd salts. Dissociation of the complexed chlorate into free chlorate is a kinetically controlled process. Chlorate could also associate with the stuff present in the paper and be restricted in its diffusion. So much for chlorate graining.

With PtCl_6^{-2} , there is probably a different mechanism, for the reaction with ferrous iron, that prevents the formation of image “grain” in the highlights. From the electrochemical data (Reaction D) the reduction of PtCl_6^{-2} to PtCl_4^{-2} by ferrous oxalate is spontaneous and has a fairly large potential of +0.74V. The conversion of PtIV to PtII would consume ferrous iron and not produce image density. Reduction of the product PtII to Pt metal would consume additional ferrous iron. Since this is an electron transfer reaction, the kinetics can be quite rapid and could well be faster than the reduction of the tetrachloride complexes to produce metal. Both Pt and Pd halides are known to form oligomeric complexes, some of which have a long chain structure. Some mixed PtII/PtIV complexes form a linear structure where there is enhanced electrical conductivity along the axis of the metal atoms. The oxalate ion in the sensitizer mixture is a good bridging ligand and could help to form chain complexes. It may also help to complex the iron into the chain or keep it near by in side branches. With a chain structure, with some electrical conductivity, it is possible to do the electron transfer chemistry and not have limitations due to diffusion or the kinetics of dissociation, especially if the iron is bound to or near the chain. On the other hand, the reduction of the Pt/PdII salts to metal is, most likely, a slower kinetically and diffusion controlled process. Hence, the different image toner produced by the various developer mixtures. Tone being a function of the size and shape of the reduced metal particles. Whew!

Does anybody have any literature references to what the structure(s) of the dried sensitizer mixture might be? We know what went into the beaker, but with all of the possible exchange reactions that are possible, who knows what the dried stuff really is.

Why not PdCl_6^{-2} for contrast control? First, it is a more energetic oxidizing agent with a reduction potential of almost +1.3V compared to the +0.76V of the platinum analog. It will attack palladium metal to give the tetrachloropalladate ion (Reaction C).

Hexachloroplatinate, on the other hand, should not attack platinum metal, in the image, (Reaction E) and would preferentially react with ferrous oxalate rather than palladium metal (0.74V vs 0.14V). Purity of the hexachloropalladate salts would probably be an issue. The potassium salt is only slightly soluble in cold water with decomposition.

Now that some speculation has been put forth, it will be interesting to see if anyone come up with some good data to either support the hypothesis or show that it is incorrect and help to formulate another explanation. Myself, I think that I will head back to the darkroom and practice some alchemy and magic. To hell with the science, I got negatives of Lena's that need to be printed!

References

Handbook of Chemistry and Physics, 42nd Ed., The Chemical Rubber Publishing Co., 1960.

Oxidation Potentials, 2nd Ed., W. M. Latimer, Prentice-Hall, Inc., 1952.

Advanced Inorganic Chemistry, 3rd Ed., F. A. Cotton and G. Wilkerson, John Wiley & Sons, Inc., 1972

--end--