

THE LONGEVITY OF PLATINUM / PALLADIUM PRINTS, A SYNOPSIS

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To the readers of this article

Please note I am not a practitioner of the beautiful art of Platinum / Palladium printing **yet**. I am an analog photographer living in the Netherlands shooting 35mm and 4x5 large format and printing and toning silver gelatine photos.

So why write on something as important as the longevity of Pt/Pd prints when I don't even create them? Well, besides some plans for "going alternative" sometime in the future, I just have a strong interest in anything related to analog photography, which includes alternative photography, and love to read up and "research" this kind of stuff. In addition, I have never found it satisfactory to just simply "know" that putting a piece of "white" photographic paper into something like developer results in a "black" photographic image, nor that something as mundane as citric or acetic acid will "stop" the "magic" going on in the developer. I want to *understand* what is going on...

Since I acquired a university degree in Biology in a previous life, I understand the basics of chemistry, and this means that reading (scientific) articles about photographic processes detailing and explaining some of the chemistry is do-able.

My interest in alternative photography was also raised by endeavours in the field of toning silver gelatine prints, realizing that there are parallels connecting the chemistry going on in there, and those in alternative processes, for example the creation of the Prussian Blue pigment that forms Cyanotypes, that is also created by blue toning a silver gelatine print.

INTRODUCTION

While Platinum / Palladium prints indisputably are among the most "archival" prints, maybe only superseded by Carbon prints, and many fine examples of the turn of the 19th/20th century or before are known to survive in remarkably good condition, there are also a few concerns that I hope to shed some light on in this article. My interest in the longevity of Pt/Pd prints was raised by a number of smaller articles and remarks I read that fascinated me. While I was aware of the "nobility" of the platinum and palladium metals, meaning they are very resistant to chemical attack contrary to for example silver in silver gelatine prints, I was also aware of their catalytic properties, as for example used in car exhaust to convert harmful nitrogen oxide gasses to harmless nitrogen (N₂). Although these properties at first did not raise my attention, they did when I first read a chapter of James M. Reilly's "Care and Identification of 19th Century Photographic Prints" [1] showing a Platinum print that had created a "mirror image" onto its cover paper. The article "The platinum print: a catalyst for discussion" [2] on the Alternative Photography website (<http://www.alternativephotography.com>), raised similar interest. While this all may sound pretty insignificant, I realized there might be more going on, and started quietly wondering about the underlying processes and the consequences for the print itself.

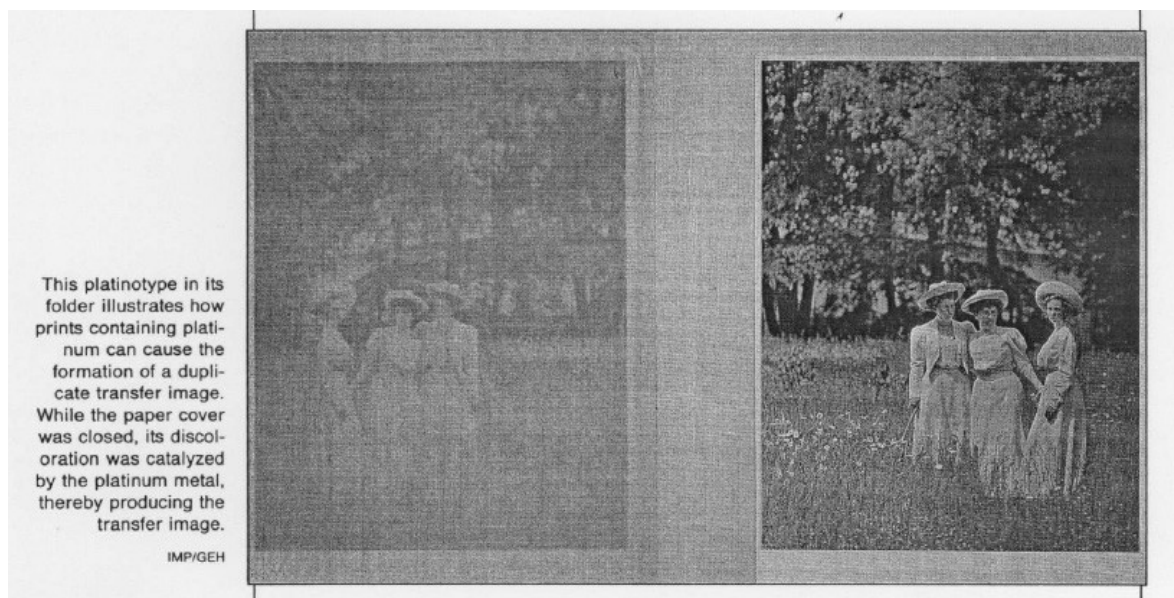


Figure 1: Mirroring of Platinotype. From [1]

A further “breaking point” for me was recently reading an article by Mike Ware about his Chrysotype process (“Chrysotype: Photography in Nanoparticle Gold” [3]) in which he wrote:

*“It has already been stated that chrysotype resembles the better-known, and at one time widely acclaimed, platinotype process (38). New chrysotypes are extremely light-fast and resistant to chemical attack; they therefore enjoy an archival permanence at least equalling, and perhaps surpassing, that of the platinotype. **The conservatorial problem which has beset all historic platinotypes arises from the high catalytic activity of platinum black, which can bring about the aerial oxidation of SO₂ to SO₃, thus causing serious acid embrittlement of the paper base by sulphuric acid formed in situ.** In contrast to platinum, nanoparticle gold has a very low catalytic activity in this respect (39), so this problem should be absent from chrysotypes. The longevity of the paper substrate will also be enhanced by the alkaline conditions of the wet processing, in contrast to the hydrochloric acid clearing baths sometimes used to process platinotypes.”*

Mike Ware is a well known expert in the field of alternative photography, and author of numerous articles in this field including a number on the Alternative Photography website.

And another remark in the article “Chemistry and conservation of platinum and palladium photographs” by Adam Gottlieb attracted my attention as well [6]:

*“**Due to stability problems associated with the paper base, platinum printing has turned out to yield far less permanent photographs than was thought or hoped. The state of old platinum and palladium prints is now of great concern.** Investigation into why and how platinum prints deteriorate has been based exclusively on the study of existing prints, most of them several decades old (Rempel 1987; Reilly 1986; Flieder 1985; Norris 1985). The tests described below offer additional insights into the impermanence of platinum and palladium prints.”*

These significant remarks spurred me to do some more literature research on especially paper longevity and start a discussion on the Analog Photography Users Group website (APUG - <http://www.apug.org>), the results and conclusions of which are summarized in this article.

Please note this article is just the result of a quick survey, not a full blown research project. Nonetheless, since Mike Ware contacted me after reading my discussion on APUG and shared some of his thoughts on the subject, and was also kind enough to review this article before publication, I am pretty sure the basic conclusions and recommendations are sound.

I will also try to include some of the sources and scientific literature I read. Just be aware that the content and some of the chemistry may be hard to understand, as some of the original scientific articles are quite complicated.

THE LONGEVITY ISSUES OF PLATINUM / PALLADIUM PRINTS

Despite the noble metals themselves being virtually indestructible (only a combination of nitric and hydrochloric acids, also known as “aqua regia”, will dissolve them), both true Platinotypes (100% Pt), Palladiotypes (100% Pd) and mixtures thereof, *can* suffer from archival permanence or longevity issues. The main issue is not with the metals and image itself, but with threats to the **paper base**.

So understanding the issues with Pt/Pd prints starts with a basic understanding of paper. Since paper’s main constituent is cellulose, a basic knowledge of cellulose may be useful.

What is cellulose?

Wikipedia says:

“Cellulose is an organic compound with the formula (C₆H₁₀O₅)_n, a polysaccharide consisting of a linear chain of several hundred to over ten thousand β(1→4) linked D-glucose units.

Cellulose is the structural component of the primary cell wall of green plants, many forms of algae and the oomycetes. Some species of bacteria secrete it to form biofilms. Cellulose is the most common organic compound on Earth. About 33 percent of all plant matter is cellulose (the cellulose content of cotton is 90 percent and that of wood is 40-50 percent).

For industrial use, cellulose is mainly obtained from wood pulp and cotton. It is mainly used to produce paperboard and paper; to a smaller extent it is converted into a wide variety of derivative products such as

cellophane and rayon. Converting cellulose from energy crops into biofuels such as cellulosic ethanol is under investigation as an alternative fuel source.” [4]

What this essentially tells us, is that cellulose and thus paper, are related to plain sugar, the one you drop in your coffee... (polysaccharides is a more difficult word for “sugars”). Just like sugar, cellulose is built up of interconnected glucose units (molecules), which give it its structure. Contrary to sugar, cellulose consists of very long chains of glucose molecules. While sugar only has two, cellulose typically has from 300 to up to 10.000 “units” of glucose connected to each other in a long chain [4]. In addition, these long chains themselves are also interconnected by what are called “Hydrogen bonds” [5].

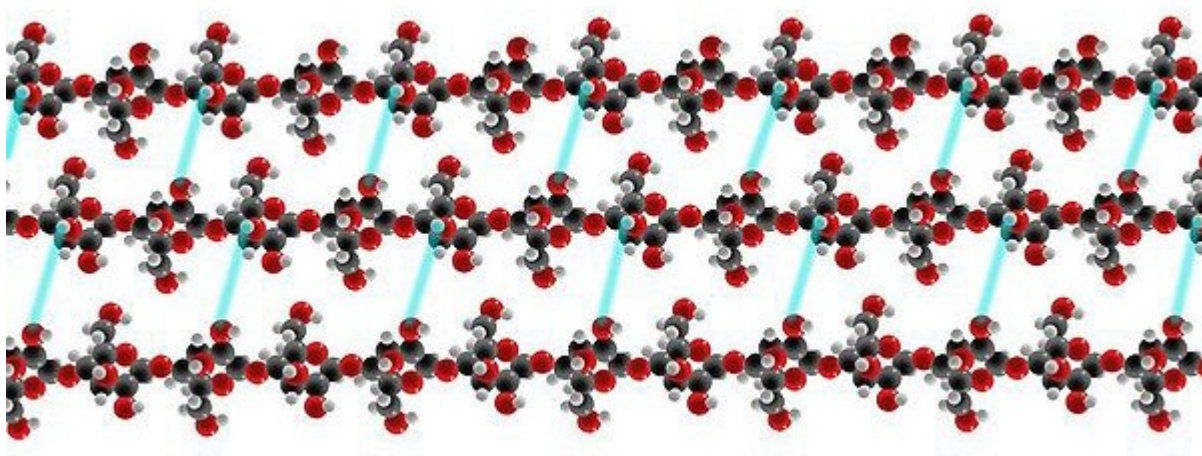


Figure 2: Structure of cellulose. Blue lines are hydrogen bonds between cellulose chains. From Wikipedia [4]

To put it simply: Paper consists of a web of cellulose fibres derived from wood, cotton or some other type of plant material. Cellulose fibres consist of long chains of glucose, a form of sugar.

Wikipedia also tells us:

*“Cellulose has no taste, is odourless, is hydrophilic, is insoluble in water and most organic solvents, is chiral and is biodegradable. **It can be broken down chemically into its glucose units by treating it with concentrated acids at high temperature.**” [4]*

This last remark is important, as it explains much of the longevity issues with iron based alternative processes like Platinum / Palladium prints.

THE THREATS TO A PT/PD PRINT

There are **four** main threats to Platinum prints, and **three** to Palladium prints, the difference caused by the lesser catalytic activity of Palladium:

These are:

*** 1) Acidification of the paper through the catalytic activity of platinum, causing embrittlement of the paper.** The catalytic activity of platinum causes air born SO₂ gas to be converted to SO₃ and ultimately sulphuric acid (H₂SO₄) [3]. Acidification leads to the breakdown of cellulose, as it splits the chains, a process called *depolymerisation* in the world of chemistry. Cellulose is the main component of wood and paper.

NOTE: Although this topic of Platinum / Palladium print acidification is in dire need of proper scientific research, according to Mike Ware he has no evidence nor read of similar catalytic acidification in 100% Palladium prints, probably due to the much lesser catalytic activity for this reaction, if at all... However, if anyone knows of research in this field, or (historic) Palladium prints suffering from acid triggered embrittlement, **please contact Mike Ware** (<http://www.mikeware.co.uk>).

Mike Ware **has** done a preliminary test for this acidification effect with 100% Platinum prints, see below.

"Many years ago, I supervised a "quick and dirty" unpublished experiment to test the general idea:

A piece of cellulose paper was half-coated with platinotype sensitizer, exposed, and fully processed to produce maximum density of black Pt.

It was cut into four pieces, two white, two black.

One white and one black piece were separately macerated in a liquidizer, and the pH of each measured instrumentally as a 'control'.

The other white and black pieces were exposed to an atmosphere of sulphur dioxide gas (ca. 1 atmosphere) for 3 days in a closed vessel.

These two were then 'pulped' and their pH's read.

The pH results were:

Controls: white paper 6.3 black Pt 6.1

SO₂ Gassed: white paper 4.5 black Pt 2.6

These rough figures seem to provide evidence that 'platinum black' catalyses acid formation in the paper.

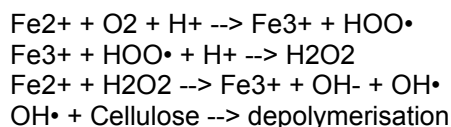
If you assume a sort of concentration/time reciprocity law for the "gassing" (I have no evidence that this is valid!) it suggests that 1 atmosphere of SO₂ for 3 days is about equivalent to a concentration of 100 ppm for 80 years.

This is an unreasonably high 'gas exposure' for an historic platinotype: outside levels could be about 1 ppm. Indoors maybe more.

Obviously this rough experiment needs to be better controlled and the variables explored. In particular the Relative Humidity of the atmosphere needs to be controlled, because I think the water content may prove to be a significant variable. It would also be interesting to see what happens with a pure palladium print."

*** 2) Breakdown of the cellulose in the paper base of a Pt/Pd print caused by hydroxyl radical formation as a consequence of retained / uncleared iron from the sensitizer used in Pt/Pd printing (Fe²⁺ or Fe³⁺ cations).**

The process behind this is about the following (from [7]):



Where OH[•] is a highly reactive hydroxyl radical, as you can see created from the remaining iron in the print. Paper is mainly cellulose, and depolymerisation means the chains of cellulose are broken down in smaller pieces, causing embrittlement of the paper.

As you can see, the reaction also requires an acid H⁺ cation to create hydrogen peroxide (H₂O₂), probably one reason more why platinum induced acidification can be detrimental to the paper base, as it additionally facilitates the depolymerisation caused by retained iron, besides the acid itself potentially causing similar issues.

The above reaction chain is also known as the *Fenton reaction* [21,22] and is commonly used to break down organic pollutants in water via oxidation [22]. Actually the hydroxyl radicals can react according to four kinds of reactions with the pollutants [22]:

- Addition: $\cdot\text{OH} + \text{C}_6\text{H}_6 \rightarrow (\text{OH})\text{C}_6\text{H}_6$
- Hydrogen Abstraction: $\text{OH} + \text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{OH} + \text{H}_2\text{O}$
- Electron Transfer: $\cdot\text{OH} + [\text{Fe}(\text{CN})_6]^{4-} \rightarrow [\text{Fe}(\text{CN})_6]^{3-} + \text{OH}^-$
- Radical Interaction: $\cdot\text{OH} + \cdot\text{OH} \rightarrow \text{H}_2\text{O}_2$

Retained iron is **not** a trivial issue. There are quite a lot of historical examples of retained iron. In fact, the Getty Conservation Institute (<http://www.getty.edu/conservation/>), states that **all** of the iron based process prints (Pt/Pd, VanDyke etc.) they investigated up to now using advanced X-ray Fluorescence (XRF) techniques showed some amount of residual retained iron, even if very good practices were employed for clearing and

washing [8]. However, very tiny amounts of retained iron will probably *not* pose a major threat to longevity of the prints [8].

*** 3) Discolouring of the paper base by formation of oxidized iron (essentially “rust”) causing yellow or even dark red stains.** The Getty Conservation Institute has witnessed Platinum prints with dark red highlights due to fully oxidized iron [8].

*** 4) Discolouring of the paper base by discolouring and break down of the paper fibres themselves.** This will mainly occur with low grade lignin containing papers made of (purified) wood pulp, as lignin is even capable of autooxidation (reaction with oxygen in the air, see [9]). However, it is likely that retained iron will or may cause similar issues even on high grade 100% cotton rag paper, via the reaction described in *issue 2*).

Nonetheless, use of high quality 100% cotton rag paper - so paper made of cotton instead of wood - should provide good chances for long term survival of the print, since this kind of paper is of a very high almost pure cellulose content. Luckily, this is already common practice among Pt/Pd printers and recommended everywhere.

This reaction is probably also responsible for the sometimes witnessed “image offsetting” onto cover paper [1,2] seen with some Pt/Pd prints, whereby a mirror image becomes visible on the cover paper. See Mike Ware’s remark below:

“Image offsetting’ by platinotypes is a well-known and characteristic effect, as illustrated by Jim Reilly and Taylor Whitney. It could be due to two things: the catalytic acid production diffusing across and degrading the opposite contacting sheet, or even to a more direct surface catalysis of the oxidative degradation by air of the polyphenolic lignin macromolecules in some wood-based papers, giving rise to quinoid structures with typical yellow-brown chromophores (same thing that causes colour of oxidised hydroquinone developers, and yellowing of newsprint). There should have been some research on this by now, but I don’t have the infra-red instrumentation needed.”

WHAT CAN BE DONE TO PREVENT ALL THIS?

You may wonder what can be done to prevent all this. Well, the following things may be of help:

- **As said, only use highest quality 100% cotton rag paper**, as it is one the most durable forms of paper with a very pure cellulose content and thus practically lignin free. Cotton rag documents have survived from the middle ages in remarkably good condition...

- **Frame all of your Pt/Pd prints behind glass, especially 100% Platinum prints.** Although it is probably very tempting to have a matt print like Pt/Pd framed without glass, it will pose a long term threat. Framing isolates the Pt/Pd print from harmful gasses, especially the sulphur dioxide (SO₂) that may be catalyzed by platinum to harmful sulphuric acid. Of course, framing only applies to photos you actually desire to have hanging on the walls of your house... For long term archival storage of other prints, archival polyester sleeves like the ones made by Secol or other brands providing archival storage materials, will provide adequate protection by excluding some of the atmosphere’s influences.

Luckily, SO₂ emissions have gone down considerably over the past 20 years or so in the West (see the figure below for the Netherlands showing a few microgram SO₂ / m³ air on yearly average basis), meaning current conditions are unlike the Victorian industrial age smog ridden cities [10], or the not so distant 1952 “Great Smog of London” that caused an estimated 4000 deaths [11] and saw a rise of SO₂ levels to an incredible 1.34 ppm or around 3000 microgram / m³ [11], more than **300 times** current *yearly averages* in most western countries. Peak values may still exist, but 500 microgram / m³ is now an absolute major alarm level in the Netherlands.

Many of the most severely affected Pt/Pd prints might date from these periods. Still, we are not down to pre-industrial age clean air, and situations in some parts of the world are undoubtedly still bad.

Zwavedioxideconcentratie

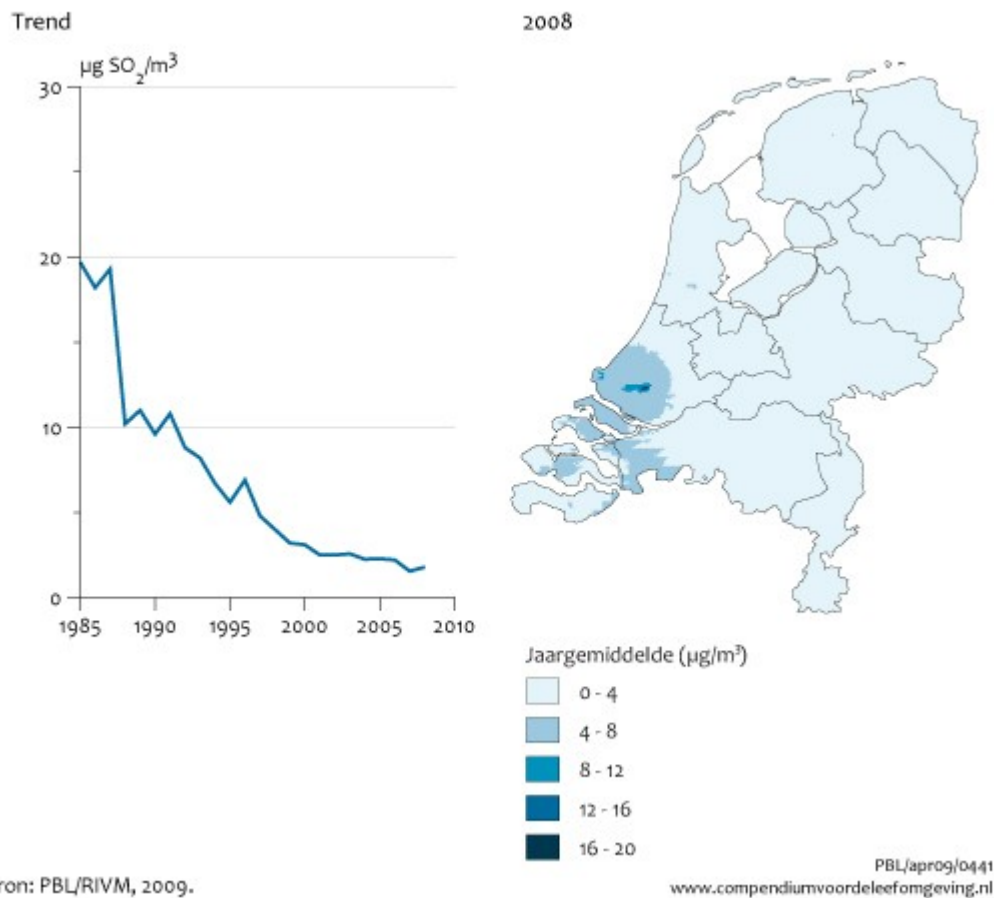


Figure 3: Sulphurdioxide concentrations in microgram / m3 in the Netherlands. PBL/RIVM 2009

- **Print 100% Palladium prints.** This is only a partial solution, but since there is currently no hard evidence that palladium facilitates the catalyst conversion of SO_2 to sulphuric acid, you will probably have reduced the chances of serious acidification as per described *issue 1*), although this is by no means a guarantee that no acidification at all will take place in the very long run, just that it will be much slower. Of course, if you desire the look of Platinum as your preferred artistic medium, there is absolutely no reason *not* to print them, and this advice is therefore a bit trivial. Your Platinum prints, if properly processed, are still very likely to outlast many other types of art.

- **Employ the best clearing and washing techniques.** Clearing in Pt/Pd printing, but also other iron based processes like VanDyke Brown, removes the iron sensitizer after exposure. This is a *vital* step in the processing of Pt/Pd prints, especially for the long term survival of the print. Any retained iron in the print may cause harm, although full removal of all iron is probably impossible (see remarks above), but safe levels are obtainable.

A good recommendation is the process described by Mike Ware in his "The Platino-Palladiotype Process" article [15]:

Chemicals required for the Processing Solutions:

- Ethylenediaminetetraacetic acid disodium salt, Na_2Edta (pH 3-4)
- Ethylenediaminetetraacetic acid tetrasodium salt, Na_4Edta (pH 9)
- Kodak 'Hypoclear' powder or sodium metabisulphite or sulphite

Treatment:

- Disodium Edta (5% w/v) 10 mins
- Rinse in water half min
- Kodak Hypo Clearing Agent (working) 10 mins
- Rinse in water half min
- Tetrasodium Edta(5% w/v) 10 mins
- Wash in running water minimum 30 mins

Mike writes about this treatment:

"The first bath is of disodium Edta, with a pH around 3 to 4, which is optimum for complexing iron(III) and is acid enough to avoid hydrolysis (of the sensitizer – edit by author) leading to yellow iron stains...The last two baths have a high pH (ca. 9) which is optimum for complexation of iron(II) and leaves the paper in a beneficial alkaline condition."

Please note though:

* It is of vital importance *to wash out all EDTA* in the final washing cycle. EDTA is what is called a "chelating agent", it binds with the iron (both Fe²⁺ and Fe³⁺) as present in the sensitizers, and forms rather soluble complexes that can be washed out. However, Iron/EDTA complexes, can still induce hydroxyl radical formation [16] as described in issue 2), and hence may still cause damage if left in the paper. It is therefore vital to properly wash the prints and remove all complexed Iron/EDTA.

* All chelators like EDTA, and the in paper conservation world used calcium- or magnesium phytate chelators, preferentially complex with Fe²⁺. In addition, Fe³⁺ can form some less soluble compounds compared to Fe²⁺ and probably binds to the cellulose fibres. See remark below by Mike Ware regarding Fe³⁺ cations and it's lesser solubility compared to Fe²⁺:

"That may be because it's quite strongly bound to the cellulose via vicinal -OH groups, - or if Fe(III) hydrolysis has proceeded very far (a complex process) it may be macromolecular "hydrated ferric oxide" physically trapped in the cellulose microfibrils. Eventually it turns into the highly insoluble mineral, Goethite FeO(OH). Any, all, or none of these hypotheses may be correct!"

This all means that if any iron is left in the print after proper clearing and washing, it is most likely Fe³⁺ species. In addition, the reaction going on in the sensitizer during exposure also produces Fe³⁺ in the process of the creation of the Pt/Pd metals.

ADDITIONAL MEASURES

For the overzealous people, there may be three additional measures that could possibly be taken to ensure maximum print longevity. Some may be applicable to other iron based processes like VanDyke Brown as well, and some definitely not, like trying to restore an alkaline buffer to a Cyanotype.

Please note these measures are experimental, just based on theoretical knowledge or general conservator treatments for paper!

Don't blame me if something turns out bad, but it does seem that there are parallels between ink corrosion and Pt/Pd print degradation, that may make it useful to consider them.

Of the three measures described here, the possible usage of Bathophenanthroline Indicator Paper for testing proper clearing of iron is probably the one making most sense for Pt/Pd printers, although again, it's usefulness for Pt/Pd printing has yet to be proven.

- **Use Bathophenanthroline Indicator Paper for testing for remaining Fe²⁺** (will not detect Fe³⁺) and thus for effective clearing in Platino/Palladiotypes. This indicator paper is used in the paper conservator world, and it seems it might potentially be a valuable new instrument for Pt/Pd printers. It seems to be very sensitive, capable of detecting just 1 ppm (part per million) iron [13].

The usage of Bathophenanthroline Indicator Paper is described in detail in a PDF document on the Ink Corrosion website (See reference [14]).

It can be bought at the Preservation Equipment website (<http://www.preservationequipment.com>) and is called "Iron Gall Ink Test Paper":

<http://www.preservationequipment.com/Store/Products/Conservation-Materials/Other-Materials/Iron-Gall-Ink-Test-Paper>

This test could serve as a Pt/Pd equivalent of a "residual-silver" test as employed by traditional silver gelatine printers for testing of adequate fixing of silver halides from silver gelatine papers.

NOTE1: Since the indicator paper only detects free Fe^{2+} cations, not free Fe^{3+} , some Fe^{3+} may still be present, even with a negative test result. Although according to Mike Ware [15], the sodium sulphite or Hypo Clearing Agent bath described in his recommended clearing sequence, will act as a mild reducing agent, converting Fe^{3+} to Fe^{2+} :

"Clearing of the residual iron compounds from the paper is improved by immersion next in a bath of Kodak Hypoclearing Agent interposed between the two Edta baths; alternatively a solution of sodium sulphite can be used. The inorganic sulphite in this tends to reduce any residual iron(III) to iron(II) which is then removed in the final tetrasodium Edta bath; the advantage is that these last two baths have a high pH (ca. 9) which is optimum for complexation of iron(II) and leaves the paper in a beneficial alkaline condition."

NOTE2: Bathophenanthroline Indicator Paper may also be of use to other iron-based alternative processes, like VanDyke Brown, for the same purpose.

- **Restore an alkaline buffer to the paper after full processing** (development). Unfortunately, calcium carbonate containing papers are **unsuitable** for most alternative processes, as the alkaline environment will destroy or at least impair the iron sensitizer, via hydrolysis of the iron(III) photosensitizer (remark Mike Ware). Normally, the much used calcium carbonate buffered artists papers provide an alkaline buffer against any acidification, protecting and prolonging the papers lifetime. These papers **can not** be used in iron based alternative processes like Pt/Pd, or must be acidified to destroy the calcium carbonate buffer. This leaves the paper without the buffer protection. There may therefore be a case for restoring an alkaline buffer after full processing, when an alkaline environment no longer poses a threat to the iron sensitizer. Restoring alkaline buffers using calcium bicarbonate buffer solutions has for example been described on the Ink Corrosion website including detailed instructions for conservators [12]. Please note that calcium bicarbonate is *not* soda or baking soda, which are respectively sodium carbonate and sodium bicarbonate and with different pH's. Calcium bicarbonate has a safe pH range of maximum 8.5 during treatment [12]. There are indications that high pH may in fact be detrimental as well to paper, just like acidification [9].

NOTE: *Do not try to restore an alkaline buffer to Cyanotypes* or similar alternative process prints that require a mildly acidic environment for optimum permanence. The Prussian Blue pigment that forms the image in a Cyanotype will be destroyed in strongly alkaline environments.

- **There may be a small case for a calcium phytate or magnesium phytate treatment as an alternative to EDTA, or as for example the second bath after a first EDTA clearing bath.** Calcium phytate and magnesium phytate have been used in the paper conservator world to remove free destructive iron from iron gall ink written documents (See reference [19] or [20] for an alternative and even possibly slightly better magnesium phytate treatment). Both leave, when properly executed, the paper at very favourable pH of about neutral, and the working solutions themselves are close to neutral. In addition, Iron/Phytate complexes seem to be almost inert [16], meaning any complex left in the paper, is pretty harmless. This is contrary to Iron/EDTA complexes, for which it is vital to properly wash them out of the paper, as Iron/EDTA complexes can still induce hydroxyl radical formation [16] that might be damaging to the paper. As a downside, the treatment with phytate may be more laborious, and Iron/Phytate may be less soluble and hence more difficult to wash out compared to Iron/EDTA complexes.

Detailed instructions for preparing and using calcium phytate can be found on the Ink Corrosion website [19]

WHAT TO DO RETROSPECTIVELY WITH OLD OR HISTORIC PT/PD PRINTS SHOWING SIGNS OF ACIDIFICATION AND / OR STAINS FROM RETAINED IRON?

The Ink Corrosion website has detailed instructions for dealing with retained iron and paper acidification which includes washing in demineralised water, calcium phytate treatment and restoring an alkaline buffer to papers as described in the previous chapter [12]. Please note that the measures described there pertain to iron gall ink written documents in the first place, and are untested / experimental for treatment of Pt/Pd prints or other types iron based alternative processes like VanDyke.

Removing iron stains from historic prints

However, to remove iron stains from historic prints that were inadequately cleared, one additional form of possible treatment deserves mentioning, as it has already been documented as an experimental treatment of historic Platinum prints having yellow/red iron stains. The treatment is discussed in the article of Gent & Rees "A Conservation Treatment to Remove Residual Iron from Platinum Prints" [18] and uses sodium dithionite in combination with EDTA for removing iron stains from Platinum prints.

Sodium dithionite [17] is a reducing agent [17], that will convert Fe^{3+} to Fe^{2+} , allowing it to be more easily washed out together with the EDTA [13,18].

Mike Ware has given some instructions about the usage and preparation of such a combined bath upon my request, see instructions below:

"Sodium dithionite becomes a much more powerful reducing agent in alkaline solution.

Sodium dithionite is unstable in acidic solution, decomposing to thiosulphate and bisulphite.

The complex formation between Fe(II) and EDTA is a maximum in alkali (~pH 10).

So to get the best reduction of Fe(III) to Fe(II) and removal of Fe(II) as chelate, one must therefore use alkaline solution.

That means, effectively, using Na₄EDTA not Na₂EDTA.

Rees and Gent started by using Na₂EDTA (possibly, they didn't have any Na₄EDTA) and adjusted the pH by addition of NaOH. They found rather little iron-removal action at pH 6.5 and much more at pH 8.5. (I won't go into the additional conservation reasons why they tried the lower pH).

My present recommendation is simple:

A solution that is 2.5% in Sodium Dithionite and 2.5% in Tetrasodium EDTA, which should result in a suitable pH around 8.5, with no need for adjustment.

Treat for half to one hour. Stronger solutions could be used, but this is economic and effective, and should be frequently changed, if one is treating a lot of work."

Especially noteworthy is the compulsory use of ethylenediaminetetraacetic acid tetrasodium salt or **Na₄Edta** instead of the more common **Na₂EDTA** in combination with sodium dithionite. **Don't use sodium dithionite with Na₂EDTA.**

Again, the usage of sodium dithionite in combination with EDTA is experimental and mainly targeted to removing already formed iron stains in insufficiently cleared historic prints, so a possible treatment to be used by conservators. It is not recommended for a regular modern Pt/Pd workflow, where the two bath clearing method described by Mike Ware and included in this article, is appropriate and should provide good results.

Many thanks to Mike Ware for sharing his thoughts on the subject, contributions and reviewing this article.

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