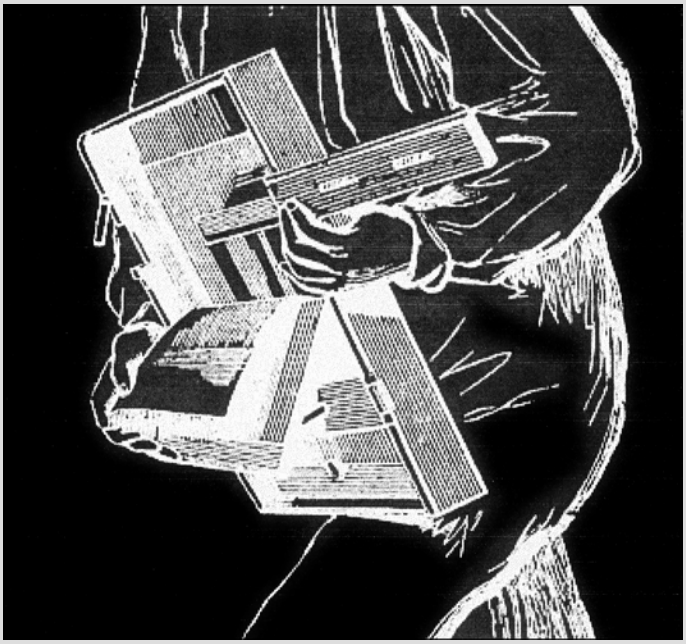
PICTO Benelux

ROGER KOCKAERTS

THE PRAXIS OF PLATINUM-PALLADIUM PRINTING



pH7 publishing - Brussels
2005

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This document contains the notes of the course "Conservation & Restoration in Photography" given by Roger Kockaerts at the Royal Academy of Fine Arts in Antwerp. Roger Kockaerts passed away in september 2019.

One of Picto Benelux's essential tasks is to perpetuate the underlying know-how necessary for the understanding and practice of historical photographic techniques, by making it accessible to the widest possible audience.

We would like to thank Nathalie, Roger Kockaerts' daughter, for giving us permission to distribute this text via Picto Benelux.

The author :

Roger Kockaerts (1931) was a photographer, gallery owner, teacher and expert in restoration and preservation- conservation of photographic documents.
He has been practicing photography since 1956, with a predilection for nature and mineral or vegetal textures; he was also interested in structures generated by computer programs and developing in random patterns. He has practiced many historical processes, especially cyanotypy and platinum-palladium printing. Around 1968 he became interested in orotone, a very old and practically forgotten process, to end up with a modernized version of his own which he called orotypy. His recent works are more inspired by photographic intention, and less by the purely aesthetic aspects.
In 1989 he created Permadocument-pH7, a specialized structure for the conservation and restoration of photographic documents. Many institutions (including the Getty Conservation Institute in Los Angeles), museums, galleries, and artists resorted to his expertise. Artists photographers from around the world using alternative photographic processes have exhibited in his gallery "Atelier pH7".
Since 1994 he has lectured at the conservation and restoration section of the Koninklijke Academie voor Schone Kunsten in Antwerp (Royal Academy for Fine Arts in Antwerp) .
Roger Kockaerts has been an active member of Picto Benelux since its inception, and until his very end.

Other publications :

"Archivale behandelingen en conserveringstechnieken voor moderne fotografische zilveremulsies".
"Techniques d'archivage pour les émulsions argentiques N&B modernes"
"Stabiliteit en conservering van fotografische kleuremulsies"
"Techniques d'archivage et stabilité des émulsions couleur"
"Identificatie, technologie en conservatie-restauratietechnieken van historische fotoprocédés.
- Deel 1: procédés gebaseerd op de lichtgevoeligheid van zilverzouten.
- Deel 2: procédés gebaseerd op de lichtgevoeligheid van ijzerzouten.
- Deel 3: procédés gebaseerd op de lichtgevoeligheid van chroomzouten.

"Historiek en praktisch gebruik van historische fotografische apparatuur. (met René Smets)
"Enkele gegevens over de historische en hedendaagse daguerreotypie en zoutdruk" (met René Smets)
"Het platina-palladiumprocédé"
"Procédés nobles en photographie: procédés photographiques basés sur la sensibilité à la lumière des sels de fer: platine-palladium, chrysotype, cyanotype, kallitype, argyrotype, ziatype", e.a.
"De kunst van het Fotoarchief – 170 jaar fotografie en erfgoed" (avec Johan Swinnen)

Picto Benelux

Picto is an an informal group open to everybody in the Benelux countries having an active interest in photographic processes developed from the very beginning of Photography. The aim is to revisit them, while respecting anyone's creative approach.

http://www.picto.info/

THE PRAXIS OF PLATINUM-PALLADIUM PRINTING

I - Introduction

The old photographic processes, known as "alternative", are based on chemical reactions similar to those of conventional silver photography.

From a chemical point of view, these processes are divided into three groups: processes based on the use of silver salts, processes based on chromium salts associated with colloids and processes based on iron salts.

The silver processes include salted paper, albumen, aristotype, and gelatine-silver bromide prints.

Chromium salt processes include gum, carbon, oil prints and their derivative processes.

Iron salt processes include cyanotype, Kallitype and the platinum/ palladium prints. The latter are the subject of this publication.

In order to fully understand the process, it is useful to explain some basic chemical concepts.

Oxides are binary compounds in which one of the elements is oxygen. They are named by adding the word oxide to the element combined with oxygen.

FeO = iron (II) oxide or its former name ferrous oxide;
$Fe_2 O_3$ = iron (III) oxide or ferric oxide.

There is less oxygen in iron(II) compounds than in iron(III) compounds, the latter having a lower valency.

A reagent is a chemical product that causes a specific reaction with another product.

II – History

THE PLATINOTYPE (1880 – 1930+)

THE PALLADIOTYPE (1914 – 1930+)

THE PLATINUM-PALLADIUM PROCESS (1970+)

In their quest for the ideal photo process, photochemists have tried all kinds of metal salts. The process based on platinum salts became popular between 1880 and 1914, but the high cost of platinum after WWI severely limited its use, much to the regret of many supporters who deplored its disappearance. For a short period, attempts were made to replace platinum with palladium, but its fate was also sealed, and the manufacture of commercial materials[1] came to an end.

Platinum was used for a long time by the first inhabitants of America before it was first mentioned in the writings of the Italian Julius Caesar Scaliger around 1500. This humanist described platinum as a miraculous metal, impossible to melt, and which could be found in what is now Panama and Mexico.

Platinum was discovered as a chemical element around 1740 by the Spanish astronomer Antonio de Ulloa, during a geographical mission to Peru under the leadership of King Philip V. While bringing platinum-bearing ore back to Spain, their ship was intercepted by the British. This explains why it took until 1748 for a publication to mention this unknown element. British scientist Charles Wood was able to isolate platinum in 1741.

The Spaniards who named this metal "platina" - a somewhat pejorative diminutive of "plata", which means silver - found it in British Columbia while extracting silver and considered it an undesirable contaminant.

It wasn't until the end of the 18th century that scientists became aware of the unique qualities of this rare and precious metal.

In 1779, the Swede Tobern Olof Bergman announced publicly for the first time that platinum was indeed a specific metal. He also proposed a new alchemical symbol, based on the combination of symbols used for gold and silver: ☽☉

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[1] BOVIS, Marcel & CHRIST, Yvan - 150 ans de photographie francaise, Editions de Francia, 1979.

The Frenchman Nicolas Anne de l'Isle (1723-1780) was the first to develop a platinum refining process. This process is still the basis of today's methods. In 1787 Count Karl Heinrich von Sichingen was the first scientist to produce potassium chloroplatinite, the basic ingredient of the platinotype invented by William Willis.

Johnson Matthey, an English company founded in 1817, began commercial refining of platinum. In 1851, the company was the leading producer of platinum, a position it still holds today...

As far as specific research in the field of photography is concerned, it was Ferdinand Gehlen who, in 1803, explored the effect of light on platinum. He discovered that a solution of platinum chloride exposed to light first yellows, before forming a precipitate of metallic platinum.

In 1831, Johan Wolfgang Deibereiner observed that platinum metal was only slightly influenced by the action of light and decided that another substance should be added to increase its sensitivity to light. After trying several substances, he chose iron oxalate.

By combining iron oxalate with platinum chloride, he found that a platinum-metal precipitate was formed. This combination is still present in the current Pt-Pd process.

Around 1832, Sir John Herschel discovered that the light sensitivity of platinum is in the violet part of the spectrum.

Around 1844, Robert Hunt reported his own experiences in his "Researches on Light"; he turns out to be the first to use platinum to form a photographic image. However, he was unable to stabilize his images[2]. Hunt was co-founder of the Royal Photographic Society.

The focus of scientific research then shifted away from the photographic applications of platinum to silver, which was more sensitive to light, although it was more sensitive to atmospheric contamination, especially sulphur. Platinum was known to be virtually indestructible and was only affected by a heated aqua regia solution (aqua regia = nitric acid + sulphuric acid).

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[2] HUNT, Robert - Researches on Light, Longman, Brown, Green & Longman, London, 1844

The relationship between the precious metals gold and platinum has led some researchers to consider the possibility of finding a platinum toning formula for silver emulsions, as it already happened with gold toning.

In 1856, the Frenchman de Carranza published a platinum toning formula in the magazine "La Lumière" and, the same year, C. Poupat published a formula using sodium chloroplatinite to tone albumen paper

A year later, Baldus described a method for toning albumen prints using platinum chloride instead of gold chloride. In 1859, it was Gwenthlian who explained his platinum toning experiments and pointed out that an alkaline platinum toning produced warm brown colours, and an acidic toning cold bluish colours[3]. That same year, C.J. Burnett was the first to show an experiment on sodium chloroplatinite and to exhibit palladium prints for the first time.

In the late 1850s, the silver process and its shift to gold toning overshadowed the idea of a universal platinum process, and it was not until the 1870s and 1880s that a usable platinum process emerged.

The first patent for a platinum process, "Perfection in the Photomechanical Process" (British Patent No. 20011, June 8, 1873), was granted to William Willis in 1873.

Willis, born in 1841, entered the service of his father after studying mechanics; Willis was the inventor of an aniline printing process for the reproduction of technical drawings.

The instability of the silver photographic process prompted Willis to look for a more permanent process and to choose platinum. He succeeded in reducing the platinum salt by using potassium oxalate.

Over the next seven years, Willis was awarded two more platinotype patents. Patent No. 2800 of July 12, 1878, referred to the elimination of silver salts and the need for a hyposulfite bath. His third patent No. 117 of March 15, 1880, was for the method that would become the classic platinotype process.

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[3] Hafey, John & Shillea, Tom - The Platinum Print, Rochester Institute of Technology, 1979.

Known as the hot-water method because of the temperature of the developer, this method consisted of removing the platinum salts from the developer and incorporating them into the paper carrier. Lead and silver salts were also removed from the photosensitive solution. This simplification made the process more controllable. These patents were collected in Luis Nadeau's excellent publication[4].

Willis was thus the first photographer to produce platinum images using platinum salts in combination with photosensitive iron salts.

After Willis founded the Platinotype Company in London in 1879, other companies began to produce platinum paper in different shades and surfaces.

Warren[5] mentioned in his handbook that Willis & Clements of Philadelphia, the "branch" of the Platinum Type Company, sold platinum paper in three surfaces: AA, a smooth paper, BB, a semi-matt paper, and CC, a paper with a more structured surface. It also mentioned the prices of platinum paper marketed in 1899:

12 sheets of 4x5 inch sheets = $ 0.45;

12 sheets of 8x10 inch sheets = $1.70;

12 sheets of 11x14 inch sheets = $3.40.

The development of Eastman Kodak's platinum paper seems to have had its own eventful history. Eastman's platinum paper, in two versions, rough and smooth, was announced in 1901 but would not have made its appearance on the market. In Kodak literature, Eastman's Water Developed Platinum Paper was also described between 1901 and 1910.

Around 1906, Eastman Kodak tried unsuccessfully to buy the firm of Willis & Clements. In 1906, Joseph di Nunzio of Boston agreed to give his Angelo platinum paper to Eastman Kodak. Finally, in July 1909, Eastman Kodak presented its Etching Sepia Platinum Paper.

Although Willis' platinum paper made it possible to create particularly beautiful prints, his process was not really accessible to the individual photographer wishing to make his own paper platinum-sensitive.

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[4] NADEAU, Luis - History & Practice of Platinum Printing, Fredericton, Canada, 1986.

[5] W.J. WARREN - The Platinotype Process of Photographic Printing, Iliffe Sons & Sturmey, London, n.d.

Two Austrian army officers, Captain Giuseppe Pizzighelli and Baron Arthur von Hübl, transformed the Willis method and published their findings in 1882, making the platinum process accessible to the general public[6].

However, in 1887, Captain Pizzighelli patented a new and different platinum process, the Pizzitype. He had found that double iron oxalate salts could be used to prepare platinum paper and that the addition of sodium oxalate to the sensitizing solution made a developing solution unnecessary.

With the addition of the developer to the sensitizing solution, the platinum salt was reduced and the image created by the platinum metal was formed during exposure. The image was then soaked in a weak hydrochloric acid bath to remove the iron, and rinsed in water to remove all the acid.

This was the first platinum P.O.P. process and was marketed as "Dr Jacoby's Platinum Printing Out Paper".

In 1892, Willis produced a platinum paper under a new patent for a cold developing process: platinum was incorporated into the sensitizing solution with which the paper was coated. Since development took place at room temperature, additives such as glycerine could be used for localized manipulation and development.

The initial period of popularity of the platinum process saw the emergence of some important associations in Europe. In 1891 the Viennese "Club der Amateur-Photographer" was founded and organized the first international photographic exhibition where photographs were considered exclusively as works of art.

In 1892, a number of British photographers left the Royal Photographic Society (R.P.S.) to form the "Brotherhood of the Linked Ring" in which an elite of amateur photographers sought to establish the foundations of "pure photography" and the techniques to achieve it.

There was a consensus to move away from silver processes and to apply new techniques, especially platinum based ones. Platinum, palladium and carbon prints were popular, and many variants of the old dichromate gelatin-based processes developed.

In 1890, Alfred Stieglitz (1864-1946) returned to America from Europe to become the champion of American photography through his lectures and demonstrations. In 1902, Stieglitz proclaimed a new American photographic vision which he called "Photo Secession", and "Camera Work" (1903-1917) became the official organ of this new vision.

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[6] PIZZIGHELI, G. & HÜBL, A. - Die Platinotypie. Wien, 1882.

With its photogravure reproductions, Camera work has set a new standard for photographic publications. The first issue was devoted to Gertrude Käsebier (1853-1934) and her platinum and gum prints.

The second issue was devoted to Edward Steichen (1879-1973).

Frederick Evans (1853-1943), the most famous and popular photographer of this period, was best known for his platinum prints of church interiors and landscapes. He was also the first British photographer to be published in Camera Work in 1903.

In France, Robert Demachy (1859-1937) specialized in bichromate gum. The Belgian photographer Léonard Missonne (1870-1943) with his oil prints was also a remarkable figure of that time.

Platinum was mainly mined in Russia, South America, Canada and Australia. Even under the best economic conditions, platinum has always been precious and expensive.

Although platinum was a relatively cheap metal when Willis invented the process, it became increasingly expensive from 1906 onwards. In 1907, platinum was 52 times more expensive than silver.

Because the price of precious metals rose disproportionately during wartime, the price of platinum soared by 1915 to the point where it became economically irresponsible to make ready-to-use platinum paper. Eastman Kodak and most other manufacturers stopped producing it in 1916.

Palladium, which was proposed as a substitute metal for platinum, has a closely related origin and history to platinum and other platinoids.

Palladium was discovered in 1803 by William Hyde Wollaston while researching crude platinum ore in South Africa. Palladium was named after the asteroid Pallas, discovered in 1801. In Greek mythology, Pallas was the daughter of Triton and friend of Athena.

Due to the scarcity of precious metals, Willis considered creating an alternative paper based on silver salts, which he called "Satista" and which was in fact a platinum-enriched kallitype paper.

Because silver has a different response to light, the resulting prints also looked different. This is what decided Frederick Evans, one of the best platinum printers of all time, to give up photography for good.

After the war, Alfred Stieglitz was the leader in the revival of platinum and palladium processes. Platinum printing was also the choice of his young protégés Paul Strand and Clarence White.

As a professional photography teacher, Clarence White mentored Laura Gilpin and Doris Ulmann. He also published a magazine called "The Platinum Print".

Platinum paper had returned to the market after World War I, but its price remained high. Edward Weston used platinum and palladium paper when he could afford it. In his "Daybooks", he mentioned that he sometimes fasted for a day in order to make a platinum print.

In England, the Platinotype Company marketed platinum paper until the late 1930s. Palladium, a little cheaper than platinum, was used to obtain images with warm colours. Iridium was also used by Irvin Penn to create even deeper black tones.

Gradually, the practice of platinum printing fell into disuse, not only because of the relative scarcity of base metals, but also because of the emergence of other art forms, more handy cameras, medium and small format film and the orientation of creative photography towards more social fields such as reportage and realism.

In recent decades, with the definitive appreciation of photography as an artistic medium and its value as an investment by collectors, platinum printing seems to be experiencing a renaissance among creative photographers.

In 1988, a ready-to-use platinum paper was reintroduced in Boston.

After a promising start, the marketing of "Palladio" paper was hampered by the gap between its price and that of kit and bulk materials. Palladio disappeared from the market around 1998.

III - The alternative photography movement

The social turnaround of 1969 led some photographers to leave the beaten track of traditional photography and to use less familiar working methods and materials.

Manual coating on unsensitized media paved the way for the adoption of archaic or forgotten processes such as gum printing, photoengraving, platinum/palladium printing among others.

Furthermore, the digital computer emerged as a creative tool, combined with or opposed to the medium of photography, and heralded the digital revolution with its incredibly fast manipulation of combinations of signs, numbers or letters[7].

A renewed interest of American universities in the history of photography has led to a large number of initiatives proposing alternative methods to the traditional silver process. Many important historical texts were reprinted in facsimile by renowned publishers, highlighting the beauty and stability of certain ancient processes.

In 1979, William Crawford published his book "The Keepers of Light" which is still read and re-read by photographers seeking information on historical photographic processes.

In Europe, the world of creative photography discovered the conservation techniques for fiberbase prints[8] , the emulsion par excellence for prestige prints, and began to turn away from the plasticized emulsions imposed on the commercial market.

A few years ago, Pizzigheli's research from the 1880s was refined and adapted in Britain by Michael Ware and Pradip Malde.

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[7] Roger COQART - *De computer in de visuele Kunst*, ICSAC (Internationaal Centrum voor StructuurAnalyse en Constructivisme), Bruxelles, 1983

[8] Roger KOCKAERTS, *Techniques d'archivage pour les émulsions argentiques N&B modernes*, édition pH7, Bruxelles, 1985.

Even more recently, the American Dick Sullivan condensed all printing-out processes into a simple process he called "Ziatype"[9].

Concerns for the durability of the photographic image and the reaction to the invasion of digital photography, with its countless identical prints made with a single click, encouraged the rediscovery of extremely stable historical manual processes, such as the carbon print and the platinum/palladium process.

How-2 & Y

THE WORLD JOURNAL OF
Post-Factory Photography

Issue #1 ....$6
reprinted April 1998
reprinted August 2001
reprinted March 2007
and April 2009

FREE-RANGE PHOTOGRAPHY INTER-ACTIVE MINITEXTS COMMENTARY ON ISSUES AND IDEAS PAST LIVES NEGATIVE THINKING FACTS SECRETS

Alternative Photography Until Now

The most frequently asked question in a workshop is, what text should I buy? The answer is, um, it's hard to say.

THE FIRST SUMMER I taught gum printing I spent a month testing papers, lights, storage, and a dozen other major details, "proving" several important, indeed trail-blazing points. Only later did I realize my "findings" might not apply beyond alizarin

Yes, Post-Factory

ON THE INTERNET THEY call it alternative photography, although the conventional wisdom has it that all silver-based media will soon be "alternative." Academia likes the term Non-silver Photography (title of the course I taught), although some of the processes use silver, which maddens the literal minded.

I used to call it crooked photography, in the sense of not straight photography until straight alternatives

Over the last decade, a large number of technical publications[10] have been devoted to the practice of alternative processes, and some specialised companies are supplying again the ingredients for these processes in general and for platinum and palladium printing in particular[11]. "The World Journal of Post-Factory Photography", by Judy Seigel, editor, New York, No. 1-9, published from 1998 to 2004, was a unique biennial publication in the world in which articles on alternative photography written by contemporary author-practitioners were published.

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[9] Zia = Sun in the language of north-american indians.
[10] See bibliography at the end of this book.
[11] In Europe: Permadocument, rue des Balkans7, B-1180 Brussel http://www.permadocument. be

APIS[12] (Alternative Photography International Symposium) is undoubtedly the largest event in the world bringing together artists specialized in alternative processes. Since 1997, thanks to the initiative of the American Richard Sullivan and the Englishman Terry King, APIS has been organized alternately in the United States and in Europe.

Richard Sullivan is also actively working on the launch of a Center for the History and Technology of Photography, which will be located in Santa Fe, New Mexico. Dr Dusan Stulik, Senior Scientist at the Getty Conservation Institute, is studying and researching, among other things, the chemical composition of historical platinum prints using the XRF (X-ray fluorescence spectrometry) technique.

In 2002, New York historian and photo critic Lyle Rexer published "Photography's Antiquarian Avant-Garde"[13] , an overview of the alternative movement and the work of some 60 international artists who practice historical photographic processes.

Specialized art galleries have been established, including the John Stevenson Gallery in New York,[14] which has perhaps the most valuable collection of platinum prints in the world. Closer to home is the "Atelier pH7" in Brussels[15], active since 1998, a European experimental art gallery specializing in noble photographic processes.

It is thanks to an ever-increasing number of contemporary artists, academic training and frequent workshops around the world that the practice of the platinum process is spreading more and more.

At the end of 2004, two Americans, Rob Shepard and Chad Jarvis, published the first issue of "Double Exposure - The Showcase for Contemporary Alternative Process Photography"[16], which aims to explain the importance of photography on hand-prepared media using alternative processes, both historically and in terms of a vision of the future of the medium of photography. It is a brilliant publication of exceptional quality that promises to become the benchmark for the alternative photography movement.

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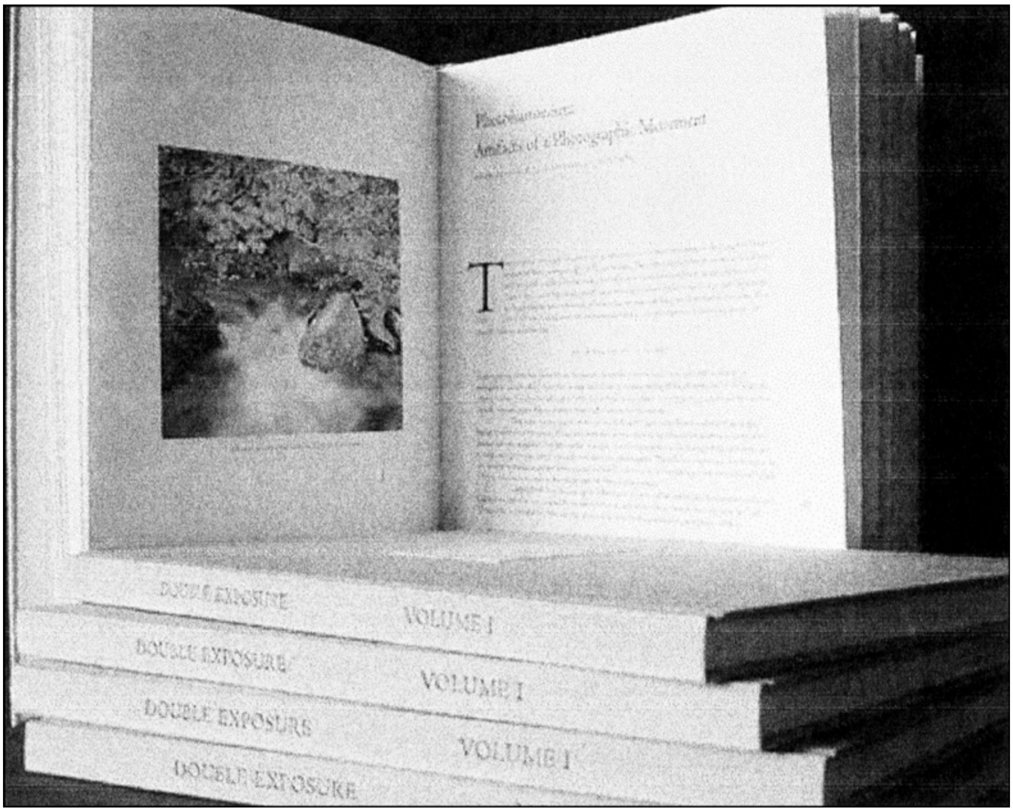
[12] http://www.bostick-sullivan.com/APIS_2005/APIS°/020Desc2005.htm

[13] Lyle REXER - *Photography's Antiquarian Avant-Garde: The New Wave in Old Processes*, New York, Harry N. Abrams, 2002, 160 pages.

[14] http://www.johnstevenson-gallery.com/

[15] http://www.permadocument.be/texte/LF/LF-menu/LF-at.html

[16] Rob Shepard et Chad Jarvis - *Double Exposure – The Showcase for Contemporary Alternative Process Photography*. 2004



Currently, the use of the Internet makes it easy to obtain the necessary materials and products, as well as information on the latest developments in the field through specialised websites[17] , mailing lists[18] and forums.

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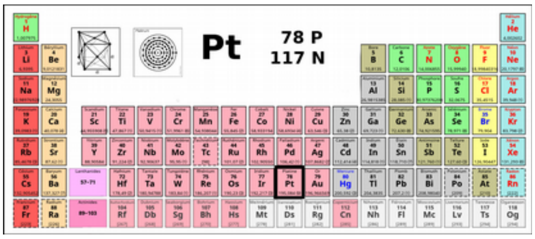
[17] http://www.alternativephotography.com
[18] ALT photo list, alt-photo-process-1@sask.usask.ca

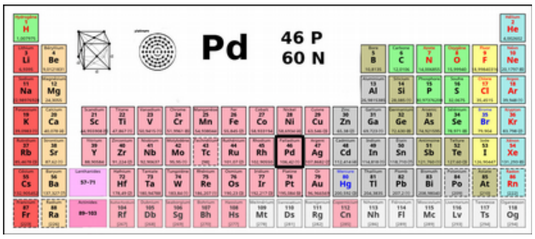
IV - Platinum-Palladium Comparison

Platinum and palladium are relatively inert heavy metals, with great similarities and small differences.



Platinum is a chemical element with the symbol Pt and atomic number 78. It is a grey-white transition metal. A transition metal is an element in Block D of the Periodic Table of the Elements[19].

Platinum is a ductile and malleable metal that has a beautiful silvery-white sheen, is resistant to corrosion by cyanide, halogens, hydrochloric acid, and does not oxidize in air. As this metal is harmless to humans and does not tarnish quickly, it is perfectly suitable for making jewellery. In addition, its good resistance to high temperatures and stable electrical properties are remarkable, which explains why platinum is widely used in industry. The only acid in which platinum dissolves is aqua regia (Hcl + HNO3).



Palladium is a chemical element with the symbol Pd and atomic number 46. It is a silver-white transition metal.

Palladium is a silvery-white soft metal that chemically resembles platinum; it does not react with oxygen in the air. It has the lowest density and lowest melting point of the platinum group metals. It is soft and easy to work with when heated, while its hardness and stiffness increase sharply at lower temperatures. Palladium reacts strongly with sulphuric and nitric acids, but dissolves only slowly in hydrochloric acid. The metal has the unusual property of being able to absorb up to 900 times its own volume of hydrogen at room temperature, making it highly suitable for industrial hydrogenation reactions.

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[19] http: / / nl.wikipedia.org/wiki/

In the resulting image, palladium, compared to platinum, is :

- – cheaper;
- – warmer in colour;
- – easier to solarize;
- – characterized by a wide range of densities, thus requiring a contrasting negative ;
- – deeper black, with a higher Dmax.

Mixing, coating and development are identical. In fact, most users mix the two metals. A mixture of 50% platinum and palladium results in prints that are almost indistinguishable from pure platinum prints.

The tone of a platinum print is cooler and more suitable for certain turning techniques. However, the tones of a Pt-Pd print are controllable by the choice of developer. The most significant difference, however, is the price.

Pt - Pd mixes

100 to 80% Pt: gives a rather cold and black image; one hardly notices any difference between these mixtures.

50% Pt: gives a pure white and well defined contrast; percentages >50% are rarely used.

25 to 35% Pt: gives perhaps the most beautiful image substance for most paper supports; for textile supports, the limit is between 10 and 30% Pt.

10% Pt: gives a warmer image with less contrast and more limited light sensitivity.

100% Pd: produces high lights with a pale pink tint that do not clear as easily.

V – Characteristics

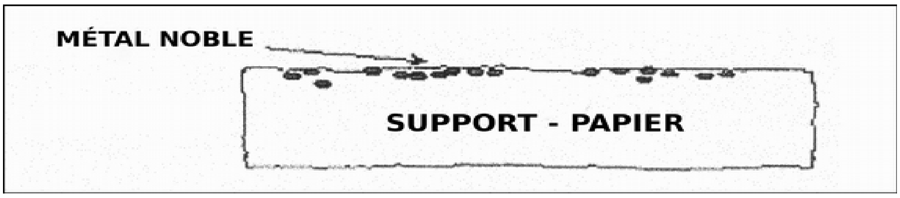
The platinum and palladium salts used in platinum prints have a low sensitivity to light. Therefore, a more light-sensitive reagent should be used. Iron (III) oxalate is best suited for this purpose.

Exposing a sheet of paper coated with iron oxalate to UV light reduces the iron salt and produces a vague image formed by the iron (II) oxalate.

This iron salt has the property of decomposing the platinum salt mixed with the iron salt and causing a black deposit of platinum metal as soon as the paper sheet comes into contact with an oxalate solution (e.g. potassium oxalate). The platinum salt is therefore not directly affected by light and its decomposition is only a consequence. This transformation can be described as "development" for the purposes of a good understanding. The removal of the undissolved iron salt is therefore called "fixing". Nowadays, this is usually done in an EDTA solution (e.g. sodium salt tetra-ethylenediamine tetra-acetic acid). The remaining image consists of finely divided platinum metal.

Platinum prints have a very delicate tonality. Under a pocket microscope (30x), the image gives the impression of being on and amongst the paper fibres.

Platinum prints have an absolutely matt surface; there is no reflection at any angle.



A developed and cleared print consists of finely divided metallic platinum particles, located between the fibres of the carrier paper. As this is a single-layer structure, there is virtually no emulsion. Once flattened, the print remains completely flat, so there is no need to glue it to a rigid support.

The Pt-Pd process is a contact print. Exposure to ultraviolet light produces a very wide range of greys.

The self-masking of shadows, characteristic of such a process, makes it possible to obtain details in the highlights without saturating the shadow areas. When a negative exposure is made, shadows appear first.

As a result, the darkest areas never become as black as with a silver print, where blackening is caused by development.

Platinum and palladium are more stable metals than silver.

The Pt-Pd print is as stable as its substrate. With manual coating, a wide variety of paper types are available. The mounting board can be perfectly adapted to the print.

No darkroom is required for platinum prints; all preparation and development steps can be carried out under existing indirect artificial light.

Contrast can easily be controlled by the composition of the sensitive layer or, in the case of ready-to-use platinum/palladium paper, by adding hydrogen peroxide to the developer.

The main disadvantage of the process is its cost price.

It is not possible to directly enlarge the image. A negative of the same size as the final image must be used.

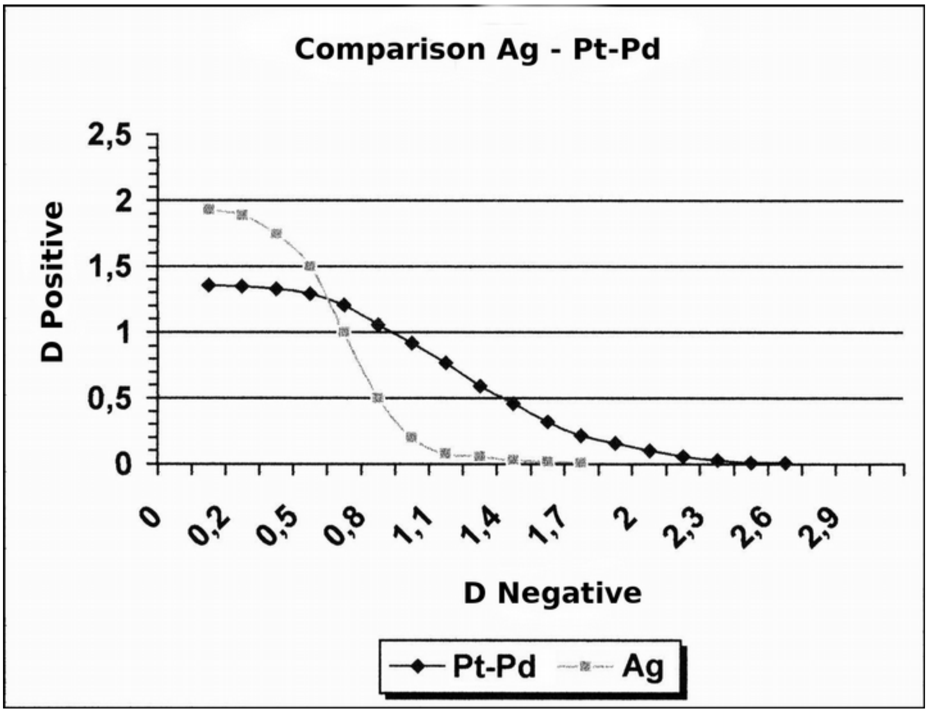
The process, although very simple, takes a very long time.

Darkroom interventions, such as pushing or holding back details of the image, are rarely used in the Pt-Pd process because of the relatively long exposure times. However, this type of intervention is perfectly possible. Local interventions are generally used when creating the enlarged interpositive or negative.

When comparing the silver process with alternative processes, it should be noted that none is really better. If a decision is made to adopt an alternative process such as, for example, pt/pd printing, and to bear the additional difficulties and costs, this decision must be dictated by factors other than the simple desire to be "different".

The sensitometric curve of fiberbase paper presented below shows very well the characteristics and limitations of the silver process:

a deep black with a reflection density of about D=2.0; a toe showing a rapid transition from white to a well-defined texture, leaving little room for the representation of subtly shaded white values ;



the transition between these extremes is abrupt, indicating a low contrast with a range approximately equal to Dmax-Dmin=0.85.

VI - Conservation – restoration

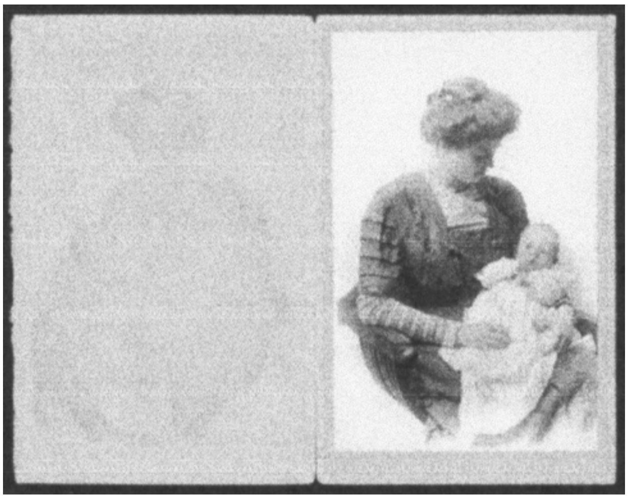
Platinum prints are particularly durable. They do not oxidize in contact with the ambient air. Discoloration effects due to light exposure are limited to the natural yellowing of the cellulose fibers that make up the paper support. This can be observed on historical platinum prints. The image shows no evidence of fading, but the paper support is less elastic and is usually yellowed.

The causes of these alterations are diverse. The poor quality of the paper used plays a role, but so do the residual transformation products. Rinsing too short leaves behind residual products that accelerate the damage to the paper support and cause yellowing.

A recent restoration study suggests that residual iron salts (as well as rust stains) can be removed from platinum prints by treatment with EDTA. In addition, freckles are drastically reduced in this way.

Gottlieb[20] carried out a thorough study of the chemical characteristics of platinum and palladium processes with respect to their conservation properties.

The acidity of a recent platinotype is around pH=3.8, which is very acidic. In addition, the properties of the platinum metal are largely responsible for the alterations. This metal is a chemical catalyst that causes, among other things, the degradation reactions of the cellulose of the paper support, but also of the paper material that has come into contact with the platinum image.



We are thinking here of leaflets and/or protective paper in albums. One then clearly notices an image transfer from the photo.

In order to protect them from damage caused by mechanical or accidental handling, it is recommended to store the mounted prints in an acid-free storage box. This should preferably be of a size suitable for the formats of the mats used.

This will also protect the quality paper support from atmospheric contamination and contact with harmful materials.

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[20] http://aic. stanford edu /jaic] articles / jaic34-01-002 indx. html

VII – THE MANUAL PLATINUM-PALLADIUM SENSITIZATION PROCESS

Traditional manual coating method

The hand coating of platinum-palladium paper is in fact a fairly recent development, born out of necessity and not out of any advantage over industrially produced ready-to-use paper.

The vast majority of existing platinum prints were made from paper that was commercially available at the time.

Below is a description of the original process and its technical data, which have been published since the invention of the process.

1 – Chemicals used

Oxalic acid - - $C_2H_2O_42H_2O$

Harmful in contact with skin and if swallowed. Keep out of reach of children. Avoid contact with skin and eyes. Spilled acid is sprinkled with calcium hydroxide and/or sodium bicarbonate. At the end of the reaction, it can be removed with a damp cloth and rinsed with water.

Potassium chlorate - $KClO_3$

This is an oxidizing agent. Do not approach it with organic solvents, ammonium salts, carbon and finely divided metals to avoid spontaneous combustion. If mixed with flammable substances, there is a risk of explosion. Harmful by inhalation and ingestion. Keep out of reach of children and away from food, drink and ignition sources. Do not smoke!

To remove small amounts of oxidizing compounds and flammable substances, mix with solid reducing agents such as sodium thiosulfate or sodium sulfite. A small amount of water is then added while stirring. After neutralisation, the liquid can then be drained off.

It is used, in very small quantities, as a contrast agent in the photosensitive solution of the Pt-Pd process.

Potassium chloroplatinite - K_2PtCl_4

Potassium chloroplatinite comes in the form of a red powder or a needle-shaped crystalline substance. It is a dangerous poison. Repeated contact with platinum salts causes dermatological and respiratory allergies. Repeated inhalation causes asthma. When processing platinum salts, wear glasses and gloves and a dust mask.

Potassium chloroplatinite is normally used in a saturated solution of 5 g per 100 ml of water at room temperature. At the concentration used in the Pt-Pd process, it is essential to heat the solution to maintain the salt in solution without crystallization. Crystallization produces grainy, uneven prints.

Sodium Chloropalladite - Na_2PdCl_4

Same hazards as for platinum salts. Chloropalladite is particularly hygroscopic and should be stored in a sealed bottle.

Palladium chloride - $PdCl_2$

Palladium chloride is toxic in contact with skin and by inhalation. The photo-sensitive solution requires a lower quantity of salts than the chloroplatinite solution. It is actually a palladium chloride solution to which sodium chloride is added.

Palladium gives warmer image tones than platinum. It is about half the price of platinum. With proper technique, images can be obtained that are almost indistinguishable from platinum.

Iron Oxalate - $Fe_2(C_2O_4)^3$

Harmful in contact with skin and by inhalation. Keep out of reach of children. Strongly diluted with water, this substance can be disposed of via the sewage system. When mixing, use a dust mask and protective gloves.

Of all the chemicals used in the Pt-Pd process, iron oxalate is the light-sensitive element. When its quality is questionable, iron oxalate is responsible for a series of problems that become visible in the final result, such as low contrast, haze formation and low black values.

Normally, iron oxalate is produced by mixing an iron hydrate with iron ammonium sulphate and then dissolving it in oxalic acid.

If one is very careful, one can produce good quality iron oxalate by oneself. The problem: the hydrate, a gelatinous mass, is very difficult to wash out and usually retains sulphates and ammonia. These residues cause reactive impurities on drying.

2 – Preparation of iron oxalate

In powder form

An oxalate of the highest quality is obtained using the well-documented method of Vicente M. Vizcay Castro, described on the Jeffrey D. Mathias website[21].

The colour of iron oxalate changes according to its oxalic acid content.

- Without or with little oxalic acid: golden amber ;
- Low oxalic acid: yellow to yellow-green;
- High amount of oxalic acid: fluorescent green.

Iron oxalate powder keeps very well. In a well-sealed jar, with a capsule or a silica gel sachet, it can be kept for more than 10 years.

Some printers modify the original formula:

- by adding a 3% solution of hydrogen peroxide, which converts minute quantities of iron (II) oxalate into iron (III) oxalate and acts as a preservative;

- by adding oxalic acid; this has the effect of decreasing sensitivity to light and increasing contrast;

- by adding an emulsifying solution or a wetting agent: e.g. gum arabic, polivinyl alcohol or Tween 20; this changes the absorption properties of the paper and the spreading properties of the sensitizing solution.

In liquid form

J. Collet22 describes an easy and reliable method for obtaining ready-to-use iron oxalate .

In a 2-litre container, 196 g of iron (III) hydrate is weighed and 200 ml of distilled water is added. Mix and leave to stand for about 1/2 hour. Then 378 g of oxalic acid is added. Mix and leave to stand for 48 hours with occasional stirring. After this the mixture is normally very liquid. The mixture is filtered into two 500 ml bottles (Melitta).

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[21] http://jeffreydmathias.com/assets/fo_powder.pdf

[22] COLLET, Jacques - Palladium, stage, Paris, 1992.

This operation can take two to three days. The result is about 300 ml of yellowish-green liquid in each bottle. This iron oxalate is concentrated and must be titrated to obtain a solution of 20 to 27%.

A small sample of $w_{l(iquide)}$ (g) is taken, that is allowed to dry on a glass lid to form $W_{d(ry)}$ (g) crystals.
(C)oncentration in % = $w_d/w_l \cdot 100$

$C\ C = 27 + CH_20$

$C = 27 + CH_20$

$$WH_2O = \frac{W}{C27}$$

W = total weight of liquid iron oxalate (g)
w_l = weight of the sample in liquid state (g)
w_d = weight of iron oxalate dry crystals (g)
CH_2O = % water to be added
C27 = 27% concentration
WH_2O = amount of water to be added (ml) to obtain a 27% solution.

Then 2% oxalic acid is added and a ready-to-use No. 1 Pt-Pd solution is obtained (as in the following formulae).

Iron oxalate is rarely used outside the Pt-Pd process. Therefore, this product is not produced in industrial quantities. A lower grade, which cannot be used in the Pt-Pd process, is used in tanneries. A good quality iron oxalate can be obtained in powder form in specialized shops and can be stored for years in a sealed bottle.

3 – Testing the iron oxalate solution

Two drops of iron oxalate solution No. 1 are applied to a filter paper. The result will be a circular coloration. Wait about one minute and then apply one drop of the next solution in the middle:

– water	100 ml
– potassium ferricyanide	5 g

With an effective iron oxalate solution, the stain fades to cyan and does not disappear after a short rinse with clear water.

Too old an iron oxalate solution produces a haze in highlights, especially when using the sensitizer mixture for high-contrast negatives.

4 – Preparing the photosensitive solution

The photosensitive solution is prepared in three different basic solutions. They are mixed in specific proportions just before being applied to the paper. The containers and utensils used shall be made exclusively of glass or plastic. Contact with metal should be avoided.

Each of the three base solutions is stored in a well-corked and marked brown bottle. The bottle should preferably be equipped with a dropper pipette. These bottles should be kept away from heat and light. Droppers cannot be interchanged under any circumstances. The chemicals are dissolved in the order of the formula.

Solution n°1 (Platinum & Palladium)

• distilled water at 50°C	55 ml
• oxalic acid	1 g
• iron oxalate	15 g

Solution n°2 (Platinum)

• distilled water at 50°C	55 ml
• oxalic acid	1 g
• iron oxalate	15 g
• potassium chlorate	0,3 g

Solution n°2a (Palladium)

• distilled water at 50°C	55 ml
• oxalic acid	1 g
• iron oxalate	15 g
• potassium chlorate	0,6 g

Instead of solution no. 2, one of the contrast agents listed below can be used, taking one or two droplets to be added to the 1+3 mixture. The contrast material should always be the last ingredient added to the sensitizing solution.

Contrast Agents

Potassium chlorate

Potassium chlorate, a traditional contrast agent, is used in a 1% solution. An excess of potassium chlorate affects the paper fibre and the image, and promotes grain formation.

Hydrogen peroxide

Hydrogen peroxide in a 3% solution has no harmful effects on the paper fibre or on the image, like potassium chlorate. However, an excess of hydrogen peroxide can precipitate the precious metal from the solution.

Potassium dichromate

A 2% potassium dichromate solution does not affect the paper fibre in the same way as the chlorate solution. Potassium dichromate can be added to the sensitizing solution as an internal contrast agent and also to the developer as an external contrast agent.

To do this, it is advisable to carry out your own experiments, given the large number of parameters that can influence the result (composition of the developer, temperature, degree of exhaustion, dilution, etc.).

Sodium chloroplatinate $Na2(PtC_{16})$

If the negative requires a large amount of contrast material, there will be a risk of excessive grain formation, image uneveness and mid-tone compression. In this case, a quantity of sodium chloroplatinate can be added to the sensitizing solution.

Abney en Clark[22] mentioned this method as far back as 1898. The graph below illustrates the addition of Na2 to a total of 30 drops of sensitizer, including 15 drops of the No. 1 Pt-Pd solution and 15 drops of the No. 3 Pd solution.

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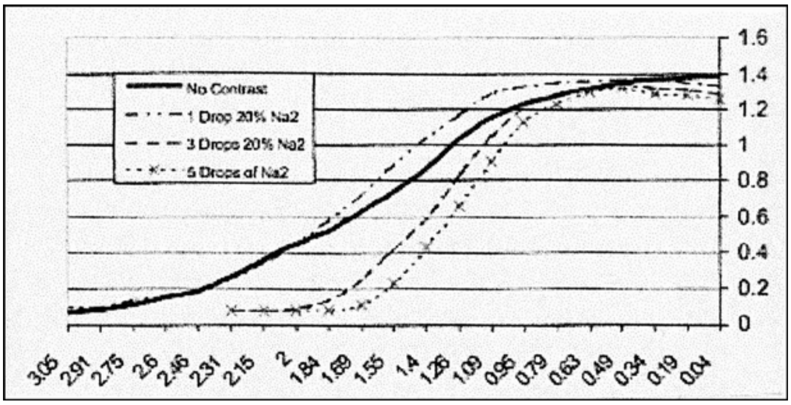
[23] Abney & Clark - The Platinotype: its Preparation and Manipulation, 1898.



It was found that by adding up to 5 drops of Na2 to this mixture, a negative can still be obtained that can be used with the palladium process[24]. Dick Arentz[25] published a contrast control system in the Pd print by adding Na2 depending on the density range of the negative used. A 2,5 to 20 % Na2 solution is added to 0,6 ml of sensitizer.
Remember that 0.05 ml corresponds to approximately 1 drop of a drop counter.

D negative	**Solution Na2 (%)**	**Quantity Na2 (ml)**
D = 1,85	2,5 %	0,05 ml
1,75	5	0,05
1,60	10	0,05
1,50	5	0,15
1,40	20	0,05
1,30	10	0,15
1,20	20	0,10
1,10 – 1,15	20	0,15

Solution n°3 (Platinum)

- Distilled water at 40°C ……………………………… 55 ml
- Potassium chloroplatinite ………………………… 10 g

At room temperature, crystallization may occur at the bottom of the bottle. In this case, heat the bottle to 50°C before using the solution.

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[24] http://www.bostick-sullivan.com/main/tech_page.htm

[25] Dick Arentz - Platinum & Palladium Printing, Focal Press, 2004

Solution 3a (Palladium)

- Distilled water at 40°C .... 55 ml
- Sodium chloropalladite .... 9 g

Solution 3b (Palladium)

- Distilled water at 40°C .... 55 ml
- Palladium chloride .... 5 g
- Sodium chloride .... 3,5 g

The photosensitive solution is measured in number of drops. The amount indicated (24 drops) in the table below is sufficient to cover a 13x18cm size. Intermediate quantities can also be extrapolated.

Density range of negative	**Solution**	**Number of drops**
high contrast	1	12
platinum-palladium (D=1,8)	2	0
palladium (D=2,1)	2	12
contrasty	1	10
platinum-palladium (D=1,6)	2	2
palladium (D=1,75)	3	12
moderately high	1	8
platine-palladium (D=1,5)	2	4
palladium (D=1,65)	3	12
average	1	6
platinum-palladium (D=1,4)	2	6
palladium (D=1,55)	3	12
moyennement bas	1	4
platine-palladium (D=1,3)	2	8
palladium (D=1,45)	3	12
léger	1	2
platina-palladium (D=1,2)	2	10
palladium (D=1,4)	3	12
très léger	1	0
platine-palladium (D=1,1)	2	12
palladium (1,35)	3	12

The stock solutions are mixed in a glass or plastic cup. The brush should be slightly moistened with distilled water (a few drops) and then wrung out as much as possible to prevent it from absorbing too much of the valuable light-sensitive solution. The Japanese "Hake" or Chinese "Jaiban" brush consists of a wooden handle on which the bristles are sewn. The advantage of this type of brush is that it does not contain any metal elements, which is suitable for most alternative processes. Its main disadvantage is that the bristles come loose during sensitization. This is avoided by spreading a drop of "Super Glue" at the junction between the bristles and the wooden handle.

5 – Coating the photosensitive solution

It is recommended that you do not touch the paper surface to be processed with your fingers. Attach the sheet of paper to a solid work surface, such as a wooden board, or a glass/Plexiglas plate. Protective gloves and an apron are advised.

The operation can be performed under yellow lighting, for example a 589 nm sodium lamp.

The brush is immersed in the photosensitive solution, which penetrates the brush by capillary action. The light-sensitive solution is spread in quick, light brush strokes.

Cover an area slightly larger than the negative to be printed. The solution is smoothed as evenly as possible. Perfect smoothness is not required, as long as enough light-sensitive solution remains between the paper fibers to react to the small amount of light passing through the negative.

Coating is stopped when the sensitive layer is uniform and the paper surface appears dry. Too much brush friction will cause streaks and local abrasions on the paper.

Wash the brush thoroughly after each use to avoid soiling subsequent prints.

The paper should be dried in the open air under low light, or better in total darkness, for about ten minutes. It is also possible to dry under moderate heat using an electric hot plate or hair dryer for about two minutes. Keep the heat source at a minimum distance of 30 cm from the surface of the paper.

Platinum-palladium paper is hygroscopic. It absorbs water from the atmosphere. If the paper absorbs too much water, you will get granular, flat highlights. Heat drying helps to partly control the moisture problem and has the advantage that the light-sensitive emulsion dries quickly before it can penetrate too far between the paper fibres. To achieve this, it is useful to dry the emulsion as quickly as possible without overheating the paper.

Several sources suggest a maximum temperature of 50°C. Higher temperatures can reduce the iron salts and cause black spots on the image.

It is recommended to use the sensitized platinum-palladium paper as soon as possible. If the platinum-palladium paper is to be stored for some time, it is recommended that it be heat-dried and stored with a silica gel capsule in a sealed envelope.

The speed of different photosensitive solutions combinations depends on the amount of potassium chlorate contained in the solution. An increased amount of potassium chlorate in stock solution #2 decreases the speed and increases the contrast.

This is an additional reason to use a drop of contrast material instead of solution #2.

According to some practitioners, a better control of tone and contrast would be obtained by using a double photosensitive layer. The result would then be a richer and more contrasting image than that obtained with a single layer.

6 – Exposure

A printing frame is used, the back of which is formed by two hinged panels, allowing visual control of the image during exposure without loss of image registration.

The Pt-Pd process has so many variables that it is difficult to recommend a base exposure in relation with the photosensitive solution used.

It is best to determine the ideal exposure time for each negative by exposing test strips or, more scientifically, by using a grey scale and a densitometer.

Since this is a printing-out process, the exposed image can be visually inspected to evaluate its exposure. To do this, the following instructions should be followed:

- always look at the image in a place protected from UV rays;
- shadow details must be well formed;
- mid-tone details should be barely noticeable;
- highlight details should not be visible, otherwise the print was severely overexposed

7 – Development

The most widely used developer since the invention of the process is potassium oxalate, $K_2C_2O_4H_2O$.

Potassium oxalate is harmful in contact with the skin and by inhalation. Keep out of the reach of children. Potassium oxalate is fatal if swallowed, even in small amounts.

A method of preparation with potassium carbonate and oxalic acid has been described by Sullivan. The basic formula contains :

• Potassium oxalate	500 g
• Water	1500 ml

The developer must be chemically neutral or slightly acidic. If necessary, add a little oxalic acid. Too much acid may cause insufficient platinum reduction.

The developer can be used at room temperature, or heated to 32-37°C, which increases its effect.

The effect of the developer is almost immediate. The processing is done either by rapid immersion or by pouring the developing bath quickly onto the print.

The slightest hesitation can leave long-lasting marks. Development should continue for 1-2 minutes at room temperature. An extension of the development time has no effect on the density of the print.

The developer can be used almost indefinitely. Some authors believe that the developer improves when used.

After a number of prints have been processed, a precipitate forms in the developer. This can be removed by filtering. The developer is then completed with a fresh bath. Warmer image colors are obtained by heating the developer. This, however, results in a reduction in contrast.

Warm tones with a mercury chloride developer

Another method of obtaining warm tones is the addition of mercury chloride to the developer. Mercury chloride is toxic and must be handled with care.

The mercury chloride developer can be used at 21°C. Increasing the amount of mercury chloride and/or the temperature increases the effect and changes the color of the image from warm black to brown and sepia. The color also depends on the paper choice.

A 10% solution is prepared by dissolving 10 g of mercury chloride in 80 ml of water and making up to 100 ml. This solution is kept in a closed bottle.

Cold tones

Blue-black tones can be obtained by adding potassium phosphate to the oxalate developer.

- Potassium oxalate ……………………… 180 g
- Potassium phosphate ………………… 60 g
- Water …………………………………1000 ml

This developer is used at 21°C.

Controlled development with glycerine

In 1900, Alfred Stieglitz, accompanied by Joseph Keiley, toured European photographic societies to demonstrate their glycerine developing system for platinum prints. This method made it possible to slow down and control the traditional ultra-fast development with potassium oxalate.

When choosing this method, it is recommended to use a robust paper that can withstand successive wet treatments. The sensitized paper is exposed to bring out all the details in the highlights.

After exposure, the print is fixed on a thick glass plate, image side up. The glass plate must be larger than the print and, after each development, it will be carefully cleaned to prevent the iron oxalate from acting on the next prints through the paper support. The print must be absolutely flat; if necessary, a quantity of glycerine should be applied to promote the adhesion of the paper support.

Using a large brush, glycerine is applied to the entire paper surface. At least four different brushes are required:

- a brush about 5 cm wide to spread the glycerine;
- a round brush with a long handle, the largest diameter of which is about the same as that of a pencil, hard enough to penetrate the coarsest types of paper without damaging the Pt/Pd layer: a kind of oil brush ;
- a fine-tip brush to work on the smallest details, for example a retouching brush;
- a brush with a width of at least 5 cm to spread the clearing solution.

Care must be taken to ensure that no hairs are deposited on the image surface. If this should happen, they must be removed immediately as they will leave indelible marks on the image.

A dry blotter of the same size is pressed by hand over the print. A light coat of developer is then applied using the various brushes; two solutions are used: an undiluted potassium oxalate solution and a solution containing 50% potassium oxalate and 50% glycerine.

A pile of thick, dry white blotters is kept at hand to remove excess glycerin or developer.

You must act without delay because a delay of a few seconds can lead to the loss of the print.

After use, contaminated blotters will be disposed of. Next, the print is covered with glycerine, pressed with a blotter, and then its surface is worked with a thick brush saturated with glycerine to penetrate the glycerine into the paper texture.

The oxalate solution, diluted with glycerin, is then applied to the parts that are to be activated first, and the image gradually appears. When dense shadows are desired, a more concentrated solution is applied. Be careful not to use a dripping brush; excess solution is removed with light finger pressure.

After the image appears, blot the image with blotting paper and immediately apply a layer of pure glycerin. The fine brush then allows you to work on fine lines.

After complete development, the print is immersed in the clarification bath and worked on with a wide brush, which improves the uniformity of the image.

8 – Clearing

Once the platinum-palladium image being developed, the remaining iron oxalate, which is still sensitive to light, must be removed from the paper fibers so that the image does not continue to blacken. This is done in two or three successive, weakly acidic solutions. The most commonly used acids are chloric acid, citric acid and tetrasodium EDTA salt. The latter two are neither toxic nor corrosive to the skin. The proportions are as follows:

- water ………………………………………….1500 ml
- citric acid or EDTA …………………………. 30 gr

After development, the prints are allowed to drain and rinsed with distilled water for 1-2 minutes. Then process them for 5 min. under stirring in the clearing baths.

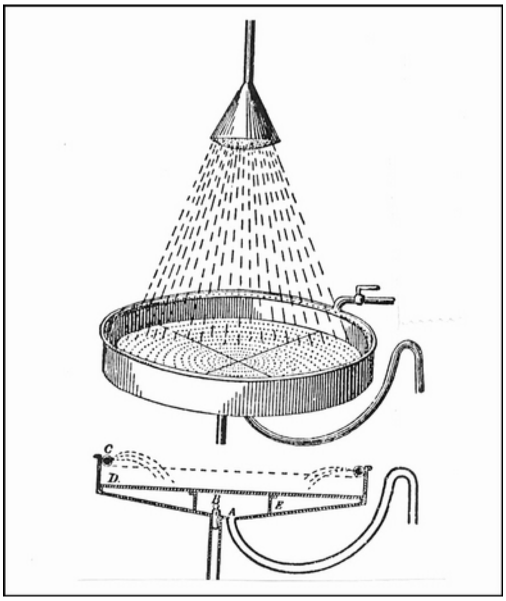
When, after frequent use, the first clearing bath turns yellow, it is replaced by the second, which is in turn replaced by a fresh solution.

Clearing is an important step in the platinum-palladium process. It will determine to a large extent whether or not the final print will turn yellow or show yellow spots after some time.

9 – Final rinse

The final rinsing of the Pt/Pd run must be done very thoroughly to remove all development and clearing contaminants that contribute to the chemical degradation of the paper fibers.

One effective method is to rinse the print in a tank of clean water for one minute and then replace the rinse water completely. This is repeated four to five times before rinsing the print in an "archival" washer.



10 – Drying

Drying is done in the open air after removing the excess water from the final rinse, by squeezing the draft between two polyester sheets.

Generally, the print will remain completely flat after drying. If not, it can be flattened in a hot press at 80°C, or under pressure between a stack of acid-free blotters.

VIII – Printing-out Pt-Pd processes

The first printing-out process was developed around 1882 by Giusseppe Pizzighelli. This process, based on the use of sodium ferric oxalate and ammonium ferric oxalate, made it possible to obtain platinum prints by inspection and not by development.

A contemporary version of this process was studied by British scientists Ware and Malde in the 1980s.

The most recent development is the joint work of Americans Sullivan and Weese, and was introduced by Dick Sullivan in 1995 as the "ziatype"[26] process

The ziatype and the Ware/Malde processes

Both processes are derived from Pizzighelli's research in the 1880s. Captain Pizzighelli was one of the forerunners of the platinum process along with Captains Abney, Hubl and Willis. Pizzighelli developed a printing-out process using ammoniumiron (III) oxalate, potassium chloroplatinite and a moistened paper carrier. The process was marketed under the name "*Dr Jacoby's Platinum Printing-Out-Paper*".

Pizzighelli experimented with different formulations based on the use of double salts and described how the addition of sodium, potassium and ammonium oxalate influenced the light sensitivity and colour of the images.

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[26] ZIA = Sun for the New Mexican indians.

In 1986, Dr. Michael Ware published a paper on a similar process, substituting ammonium chloroplatinite for the potassium version used by Pizzighelli.

In 1996, Richard Sullivan developed a system for selecting a blue-black to brown colour using palladium, lithium and/or cesium chlorides. The resulting ziatype can be described as a palladium printing system based on the Pizzighelli method in which colour and contrast are chemically controlled and the moisture content of the substrate has little influence.

Comparison

- The Ziatype uses lithium and cesium-palladium salts to chemically obtain an extended colour rendering. Colour, contrast and moisture content are virtually independent of each other.

The Ware/Malde process uses the ammonium salt of platinum and palladium. The colour depends on the balance between the moisture level in the paper substrate as well as Pd and Pt salts content.

- The Ziatype allows negatives to be printed with a density range of 0.8 to 2.0 through chemical control.

In the Ware/Malde process, the contrast is controlled by moisture, which also influences the colour.

- The Ziatype exclusively uses palladium. The use of platinum does not provide any benefits in terms of quality and permanence.

The Ware/Malde process uses platinum as one of the ingredients for colour control, which also influences the duration of the sensitising process.

- Ziatypy can be used without any problems with a very wide range of moisture levels.

The Ware/Malde process recommends a humidification chamber for strict humidity control.

- The only element common to both systems is the use of ferric ammoniacal oxalate to achieve the printing-out phenomenon that has been the essence of the Pizzighelli process since 1880.

1 – The Ziatype process

The ziatype process was recently developed by Dick Sullivan; like the Ware/Malde process described below, it is a derivative of the Pizzighelli process of the 1880s.

Pizzighelli used ammonium or sodium iron oxalate, potassium chloroplatinite, and a wet paper substrate to produce the printing-out effect. The "Pizzitype" was marketed for a short period of time and was discontinued due to technical manufacturing problems.

In the ziatype process, lithium chloroplatinite and cesium chloroplatinite, two double salts built on alkali metal composites, are used. Lithium, a light substance, is located at the top of Table I of the Periodic Table and produces a blue-black colour.

Cesium, a heavy substance, is located at the bottom of Table I and produces a brownish-black colour. Cesium is the most alkaline substance in the Periodic Table and is one of three metals that are in liquid form at room temperature.

The combination of lithium and cesium produces prints in which brown to blue-black colours can be obtained under a wide range of humidity. Ziatypy is a printing technique using only palladium, based on the Pizzighelli principle, but where colour and contrast are chemically controlled and the moisture content of the paper support plays a minimal role.

The benefits of this process include:

- it is a very versatile p.o.p. process where the quality of the image can be easily controlled at the exposure stage;
- a good match for most types of paper;
- allows the use of negatives with a wide range of contrast;
- a high sensitivity to light;
- pno need for a developer;
- produces cool, neutral blacks with palladium alone;
- a good Dmax without the use of platinum, which is very expensive;
- no solarization effect;
- all the necessary products are available as a kit.

The lithium-palladium process

The sensitizing solution

The basic recipe for the ziatype process, giving neutral grey tones, consists of two solutions: ammonium iron oxalate and lithium chloropalladite (LiPd).

Solution #1a (ammonium oxalate)

Ammonium iron oxalate	40 g
Water, to make	100 ml

Solution #1b (lithium)

Iron oxalate	13,4 g
Lithium oxalate	8,8 g
Water, to make	100 ml

A 100% #1b solution gives very warm (reddish) but rather contrasting tones.

A mixture with 50% of #1a solution and 50% of #1b solution guarantees black shadows and a wide range of densities with warm medium tones.

A mixture with 25% of a #1b solution and 75% of a #1a solution combines a wide range of densities with very delicate highlights.

Solution #1c (sodium oxalate)

iron oxalate	13,4 g
sodium oxalate	11,8 g
water, to make	100 ml

Solution #1 c (as used by Pizzigheli) gives a higher contrast than solution #1a, with a black Dmax and with medium grey tones rendered in very light brown.

Solution #2 (contrast agent)

ammonium dichromate	25 g
water, to make	100 ml

A 2%, 5% or even 20% dichromate solution in the form of droplets added to the sensitizer mixture (about 1 drop per 500 cm^2 of image area) allows a gradual increase in contrast (see table below). Ammonium dichromate increases tone separation throughout the image by improving separation in shadows without affecting highlights.

The dichromate provides a warmer image than the mixture without contrast agent, but it increases the exposure time, which also becomes more critical.

A series of dilutions of 1 to 20% can be prepared and stored in a bottle with an eyedropper. One drop in the sensitizer mixture can significantly alter the contrast. It is therefore necessary to experiment.

Solution #3a (LiPd)

• Lithium chloride	6,8 g
• Palladium chloride	9,2 g
• Water, to make	100 ml

Chamois tones can be obtained by replacing the lithium solution with a cesium solution, or by adding the latter to the basic formula (see table).

Solution #3b (CsPd)

• Cesium chloride	8,8 gr
• Palladium chloride	8,8 gr
• Water, to make	100 ml

Additives

The absorbing capacity of the paper support can be improved by adding a solution of Tween 20 (about 1 drop per 500cm^2 of image area).

Solution #4a

• Sodium tungstate	16 gr
• Water, to make	100 ml

The use of sodium tungstate gives a brown colour different from that obtained with cesium palladium and also gives soft and delicate tones with a good Dmax. In some cases, sodium tungstate reacts and forms tungstic acid. The order of introduction is critical and must be respected: FO + ST +LiPd.

Solution #4b

- Gold chloride .... 5 g
- Water, to make .... 100 ml

Using gold chloride

Gold chloride is used to obtain tones ranging from neutral grey to blue and even purple. Gold chloride is used as a metallic component of the image and not as a toning agent. A few drops of gold chloride replace a certain volume of the lithium solution in the LiPd Sensitizing Solution #3a.

The gold chloride is added after the LiPd, otherwise it will be precipitated in the oxalate solution. It is not possible to mix the gold chloride with a CsPd solution.

% Gold	Tone	Contrast
15 to 25%	neutral to cold	average to high
50%	blue to violet	high
80%	violet to lavender	very high

The exposure time increases with the amount of gold added.

Using Platinum

The hygroscopic effect of LiPd is so great that half of the metal component in the emulsion can be replaced by a #3 Pt solution based on potassium chloroplatinite, as used in the development method, without affecting the printing-out effect. A 25-50% platinum content forms a very delicate image in any image register.

Sensitizing

The sensitizing is done with a classic Hake brush or glass rod. As with the Pt-Pd print, approximately 0.5 ml of solution is used for an image area of 100 cm2. The amount of solution #1 must be equal to the sum of solutions 3a and 3b.

The method using a glass rod is much more economical. A rod should have a length corresponding to the smallest dimension of the image to be printed. The sensitizing solution is poured along the rod, which is then moved over the surface of the paper without exerting pressure. First relatively quickly: about 5 to 6 sec. per pass, and then more slowly: about 15 sec. for the last pass, taking care not to break the line of fluid visible through the rod.

The printing-out of the ziatype depends on the humidity of the paper. In very dry areas, the ideal humidity of 50-60% R.H. can be obtained by using the humidification technique, described in the Ware/Malde method, or by regulating the relative humidity of the room where sensitization is carried out. The author achieves good results by humidifying the paper support with water vapour until the paper loses its stiffness.

The paper support is then left to rest in a closed box for a few minutes to even out the water content of the paper. The relative humidity inside the humidifying box is measured with a digital hygrometer.

One-step drying

This is the best method to obtain pure black tones. After sensitizing the paper support under a relative humidity (R.H.) of 50 to 60%, let the paper rest for 2 to 3 minutes.

Dry the paper with a cold air stream directed to the emulsion side until the paper is dry to the touch (1 to 5 min.). This can be assessed by touching the sensitive side with a finger covered with a rubber protection: a smooth and satiny feeling indicates that the paper support is ready to be exposed.

If the paper substrate is dried without using forced air, uneven spots or graininess may appear in the image.

Two-steps drying

This drying method produces black to brown-black ziatypes. After drying as described above, the paper is wetted again in a humidification chamber above a saturated solution of :

Product at 20°C	*Obtained* H.*R.*
Magnesium nitrate hexahydrate	54,9%
Calcium Nitrate Tetrahydrate	55%
Sodium dichromate dihydrate	55,2%

Humidifying for two to three minutes is usually sufficient. The ideal wetting time can be determined experimentally.

Exposure

When the photosensitive layer is dry, it is exposed under a UV-rich light source. The exposure time is about three times shorter than with the Pt-Pd development process.

When exposed to sunlight, it is advisable to carefully apply a polyester sheet to the back of the paper support to maintain the water content during exposure.

Inspection

It is very important to learn how to correctly evaluate the image in the printing-out process. The orange colour of the uncleared image leaves a false impression of highlights and bright areas.

It is advisable to arrange the image correctly in the printing frame in order to be able to evaluate the most important image elements at their correct values when checking during exposure.

It should be noted that the total exposure time, interrupted by several inspections, does not correspond to a continuous exposure for the same total time. It is therefore necessary to experiment.

Clearing

After exposure, rinse under running water for at least 2 minutes. Clearing is then carried out in the same way as with the Pt-Pd development process.

The following solutions can be used for clearing:

- phosphoric acid;
- a 2% solution of citric acid ;
- hydrochloric acid (a 4% solution is the historical clearing bath) ;
- Tetrasodium EDTA, 4% solution;
- auxiliary rinsing baths used in silver photography: Kodak Hypo Clearing, Wash-Aid, Sodium Sulphite in 1% solution, etc...

In fact, all anti-corrosion agents can be used. In general, however, preference is given to a solution of tetrasodium EDTA as a 3 to 4% solution in distilled water. In many cases the EDTA solution alone is not sufficient for complete cleariing. In this case, a 1% sodium sulphite solution is added.

• EDTA tetrasodium	40 g
• Sodium sulphite	10 g
• Water, to make	1000 ml

The first clearing stage consists of a running water rinse, to remove most of the surface iron salts.

The print is then placed in the first clearing bath for four to five minutes with agitation. Between the different clearing baths, the print is rinsed in running water. The clearing has to be repeated in at least two clearing baths.

The first clearing bath is quickly exhausted and yellowed by the removed iron oxalate. It should be noted that the last clearing bath must remain completely transparent after the complete processing of the print.

The clearing is an important step in the Pt-Pd process. Incomplete clearing may result in partial discoloration of the image over time. Staying too long in an exhausted clearing bath saturated with iron salt can cause staining.

A white border around the image allows you to visually check the quality of the clearing.

After the clearing, the image is rinsed for about ten minutes. Remove the surface water by pressing the print between two sheets of polyester and air dry.

The Cesium-Palladium process

Solution #3b (CsPd)

• Cesium chloride	8,8 g
• Palladium chloride	8,8 g
• Water, to make	100 ml

Solution #3b (CsPd) is a supersaturated solution that precipitates at room temperature and must therefore be used hot. A print from a 50-50% LiPd - CsPd solution gives neutral black Dmax values with complex warm tones in the mid-grey tones and highlights. A print from a 100% CsPd solution has very warm colours with red tones in the Dmax values.

Toning

A bath composed of 50% lithium palladium + 25% of a 5% gold chloride solution + 25% sodium tungstate gives blue-black colours.

Exposure table (number of drops/solution)

Legend :

afo = ammonium ferric oxalate = solution #1

lfo = lithium ferric oxalate

sfo = sodium ferric oxalate

LiPd = lithium palladium = solution #3a

CsPd = cesium palladium = solution #3b

goc = gold chloride = solution #4b

ad = ammonium dichromate = solution #2

sT = sodium tungstate = solution #4a

afo	lfo	sfo	LiPd	CsPd	goc	ad	sT	colour	contrast
12			12					neutral black	low
12				12				warm	low
12			12			0,02		neutral	low to average
12			12			0,05		warm	average
12			12			0,2		warmer	very high
12			10		2			cold	average
12			8		4			very cold	high
12			4		8			violet	very high
12			9		3		2	green-blue	low to average
12			12				2	cold	low
12			12				3	very warm	very low
		12		12				warm red	low to average
	6	6						warm	low
	12	12						yellow - warm	low to average

2 – The Ware/Malde process

A set of instructions to obtain Pt-Pd prints with a modern economic method, using "common" (sic) materials. The method was developed by Dr. Mike Ware, in collaboration with Prof. Pradip Malde.
When applying this method, it is possible to obtain colour tones ranging from blue-black, through neutral grey tones, to rich sepia-brown colours.

Benefits of the Ware method

- iron (III) oxalate is replaced by iron (III) ammonium oxalate, which is more economical and available in pure form ;
- the new method is a true printing-out process that requires little or no development, unlike the traditional platinum process where the complete image appears only in the developer.
The sensitized paper substrate is brought to a controlled humidity level, allowing Pt-Pd images to be generated during exposure.
This procedure is easily modulated, making the use of test strips superfluous.
- The reagents and unexposed sensitizer are removed using modern chemicals: EDTA disodium and tetrasodium, which keeps the remaining paper at a high pH, without any residual iron ;
- Contrast control is performed by mixing Pt and Pd or by controlling the R.H. (relative humidity) ;
- the maximum density is higher because a soluble platinum salt is used, making the application of two coats superfluous.

Chemicals used

Iron(III) ammonium oxalate (NH4)3 ((Fe(C204)3)) 3H20

Non-volatile crystals. Also known as: ammonium ferrioxalate or ammonium trioxalatoferrate(III) trihydrate. Like all soluble oxalates, this substance is highly toxic and can cause death or serious injury (especially kidney damage) by swallowing several grams. Irritating to mucous membranes and eyes.

Ammonium (II) tetrachloroplatinate (NH4)2 (PtC14)

Previously known as ammonium chloroplatinite. Contact with this substance causes asthma and dermatitis. In case of allergies, it is preferable not to use platinum; however, palladium can still be used. Avoid skin contact with platinum-sensitized paper and its processing products. The use of rubber gloves is essential.

Metallic platinum does not present these problems, so a platinum print can be handled safely.

Ammonium (II) Tetrachloropalladate (NH4)2 (PdC14)

Is considered moderately toxic and mildly irritating or allergic. The greatest risk is inhalation of the substance when mixing powdered products.

Ammonium chloride

Palladium(II) chloride

Ethylenediaminetetraacetic acid disodium salt or EDTA disodium salt

Ethylenediaminetetraacetic acid tetrasodium salt or tetrasodium salt EDTA

Preparing the photosensitive solution

Some of the solutions used may degrade over time, the quantities recommended below are suitable for about 50 prints with a surface area of about 500 cm^2.

The iron salts solution

Dilute 30 g of ferric ammonium oxalate in 30 ml of hot distilled water (about 50 °C) while stirring. Make up to 50 ml with distilled water. Filter and store in a brown bottle, in the dark and at room temperature. This solution can be stored without time limitation.

Platinum (Pt) solution

Dilute 5 g of ammonium(II) tetrachloroplatinate in 15 ml of distilled water at room temperature. Make up to 20 ml with distilled water. Immediately pour into a bottle, filter and decant the small amount of solid yellow matter that forms. Avoid contact with air. Prépare at least 24 hours before use.
This solution will keep for about 6 months.

Palladium (Pd) solution

Dissolve 1,8 g of ammonium chloride in 20 ml of very hot (70 - 80°C) distilled water. Add 3 g of Palladium (II) chloride while stirring (dust mask!). Continue heating (70 - 80°C) until completely dissolved (approx. 1 hour). Filter and store in a brown bottle.
This solution can be stored for an unlimited period of time.

Preparing the processing baths

The processing requires solutions based on EDTA salts. The first bath is a 5% solution of disodium EDTA with a pH value of 3 to 4, which is optimal to avoid yellow stains. The capacity of this bath is about 50 prints of 500 cm2.

Clearing is improved by treatment in an auxiliary rinsing bath of the KHCS (Kodak Hypo Clearing) type. The sodium sulphite contained in this solution reduces iron (III) to iron (II), which is then removed by the next EDTA clearing bath.

The latter consists of a 5% solution of tetrasodium EDTA with a pH of approximately 9.00 which leaves the paper in a safe alkaline state.

Choice of sensitizing solution

Platinum and palladium solutions are recognizable by the colour and contrast they give to the final print; palladium gives warmer colours and a soft image with delicate reflections. This means that precise control can be exercised by mixing Pt and Pd in all possible proportions. Exposure time will be significantly affected because palladium is about twice as sensitive to light as platinum.

Caractéristiques

Solution	HR %	Speed	log H	Develop^{mt}	Colour
Platinum	32	1,8	1,2	0,9	warm black
	55	1,7	1,2	0,3	warm black
	80	1,0	1,5	0	neutral
Palladium	32	0,5	2	0,4	Vandyke brown
	55	1,3	1,9	0,2	sepia
	80	2,5	1,8	0	neutral
Pt-Pd (3:1)	32	1,2	1,6	0,6	warm black
	55	1,0	2	0	neutral
	80	1,0	2	0	neutral

Note:

– The term "Speed" is relative and mathematical and refers to average grey values.

– "logH" is the range of densities from the base fog value +0.04 to 0.9 Dmax.

– "Development" in logH values (0.3=1 f-stop) corresponds to the density range where 0 = full print.

These parameters are only indicative and will change when another paper support is used.

Preparing the sensitizing solution

Mixing is prepared under tungsten light and at room temperature. The amount of solution required depends on several factors: the type of paper, the surface to be sensitized and the sensitizing method play a significant role.

For a platinum print, equal volumes of iron and platinum salts are mixed: before sensitizing, the solution is left to stand for 1 hour at room temperature in total darkness. This maturation time improves the black tones.

For a palladium print, equal volumes of iron and palladium salts are mixed; this solution can be used immediately.

For a Pt + Pd print, the chosen Pt + Pd combination is mixed with an equal volume of iron solution; before sensitizing, the solution is allowed to stand for 1 hour at room temperature and in complete darkness.

Sensitizing

All sensitizing manipulations can be carried out under tungsten lighting. Fluorescent lamps and daylight are avoided.
The ambient temperature should be between 18 and 22°C. If the temperature is lower, the sensitizing solution may crystallize; if the temperature is too high, the solution penetrates too deeply into the paper fibers.

Paper stored at low humidity (<50% RH) will absorb too much solution and result in an uneven emulsion layer. When working in a very dry climate, it may be necessary to humidify the paper to a relative humidity of 70-80% before sensitizing.

Drying

After sensitizing, the paper is placed horizontally until the gloss on the surface of the sensitive layer disappears. Then it is dried in a hot air stream (40°C) for about 10 minutes or for about 1 hour at room temperature.

The paper support is examined under raking light; the formation of crystals on the surface may scratch the negative.

Conservation

The sensitized paper should be used within a few hours. When it has to be stored for at least 6 months, fogging can be avoided if a light-tight container with a RH < 10% is used, in which a silica gel sachet is placed.

Humidification

Controlling the moisture content of the sensitized paper plays an important role in the printing-out process.

As shown in the table below, optimal results are obtained between 50 and 80% RH (relative humidity). Below 50% RH, partial blackening occurs, which must be compensated for by additional development. Above 80% RH, the maximum density may decrease due to too deep penetration of the sensitizing solution into the cellulose fibers.

The best control of the moisture content is achieved when using a water tank with a lid, in which the paper sheet can be placed horizontally above the saturated solution. It is important to always allow for an excess of ad hoc product in the saturated solution.

Product at 20°C	H*R obtained*
Magnesium chloride hexahydrate	33,6%
Calcium chloride	45,0%
Magnesium nitrate hexahydrate	54,9%
Calcium Nitrate Tetrahydrate	55,0%
Sodium dichromate dihydrate	55,2%
Sodium chloride	75,5%
Ammonium Chloride	80,0%
Water	100%

The minimum humidification time is 30 minutes; the maximum duration is not critical and can last for several hours. However, when pure water is used, this time is very critical and should be between:

- 5 to 20 min. for warm tones;
- 30 to 40 minutes for cooler tones;
- 1 hour will result in a reduction of the maximum density.

A paper that is too wet can cause a chemical fog or irreversible yellow iron hydroxide stains and, moreover, remain stuck to the negative.

Exposure

As usual, under a UV-rich light source. To avoid sticking, it is recommended to place a transparent polyester sheet between the sensitized paper and the negative.

Correct exposure can be achieved by inspection without the need for test strips. It should be noted, however, that slight development may occur during wet post-treatment.

Under optimal print-out conditions (RH = 80%), exposure is maintained until the desired result is achieved.

Clearing

1. 5% disodium EDTA solution 10 min.	10 min.
2. Water rinse	30 sec.
3. Auxiliary rinse bath	10 min.
4. Water rinse	30 sec.
5. 5% tetrasodium EDTA	10 min.

This treatment mainly concerns palladium and Pt + Pd prints and can be carried out under tungsten lighting. For platinum prints where the highlights show too little detail, it is preferable to use a traditional Pt developer as a first bath, e.g. a 30% potassium oxalate solution (toxic!). A single drop of Pd in the sensitizing solution can remedy this problem.

An additional processing technique is to allow evaporation from the paper sheet (40°C) for 1 to 2 minutes before clearing it.

Final wash

For at least 30 minutes in running water.

Drying and finishing

The usual. The quality of the clearing can be judged by using blue light to detect any residual yellow iron spots.

Contrast control

First of all, it should be noted that there is no substitute for a perfect negative with a correct density range. Oxidizing substances such as potassium chlorate or hydrogen peroxide are not recommended as they only degrade the highlights, causing an imbalance in the image. The best way to proceed is to use the humidification method already described.

IX – Ready-to-Use Pt-Pd Process

In the recent past a ready-to-use Pt-Pd paper has been marketed and manufactured by the American company "The Palladio Company". It was relatively successful from 1988 to 1997[27].

In order to improve its storage capacity, the paper was heavily dried and a quantity of silica gel was provided in each package. Completely dry, the paper is more or less inert and not very sensitive to light; it must reach a certain degree of humidity to develop its maximum density.

This is done by means of ultrasonic misting or by allowing steam to act on the paper for 50 to 100 seconds.

After being moistened, the sheet of paper is left to rest for a few minutes to even out the moisture content throughout the sheet.

Exposure

Before exposure, the palladium paper has a yellow-orange colour. At a distance of 10 to 15 cm from a battery of solarium-type BL tubes, and depending on the density of the negative and the temperature of the developing bath, the exposure time can be estimated at 3 to 12 minutes.

Development

Two Palladio brand developers were proposed: the "standard" developer, corresponding to the traditional potassium oxalate formula that generates warm black colours, and the "cold tone" developer, or ammonium oxalate formula, to obtain cooler and more contrasting prints.
A "brown tone" additive made the proofs browner and softer.

The developer had to work without agitation for 4 minutes. It was not possible to influence the contrast by manipulating the development time.

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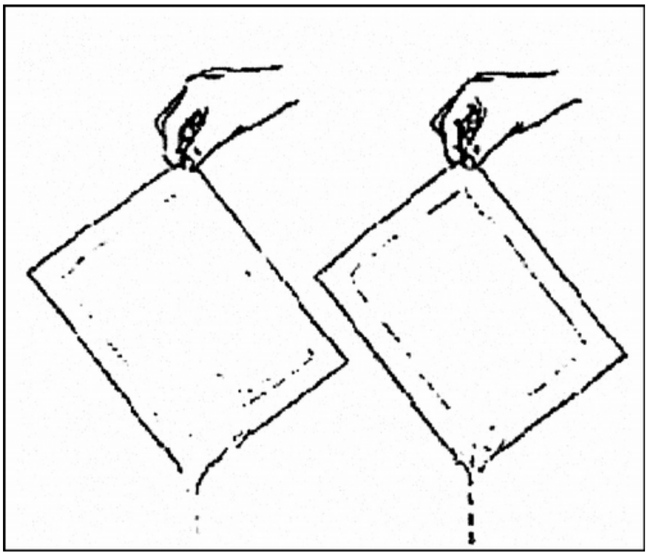
[27] < http://www.personal.psu.edu/users/w/c/wcrl12/palladiopaper/index.htm>

Instead, a quantity of 3% hydrogen peroxide was added to the developer. 1% peroxide did correspond to one paper grade, and 3% or more could be added when looking for higher contrast.

Clearing

After having allowed the developer to drain from it, the print is rinsed with water for 1 to 2 minutes. The clearing bath is EDTA-based and consists of three consecutive baths in which the print is rinsed for 4 to 5 minutes. The most effective way of stirring is to lift the sheet of paper at an angle and allow it to drain as shown in the following figure. This is done at each corner and continuously for 1 minute.



The final wash and drying is done in the traditional way.

X – Platinum-Silver Processes - The Satista Process

In terms of image quality, platinum-silver processes can compete with platinum prints but cannot match their permanence.

Brownish silver images consist of very small metal particles of about 20 nanometres; the colour depends on the absorption of specific light beams, depending on the shape, size and amalgamation of these metal particles and on the chemical environment.

These tiny image fragments are very sensitive to chemical degradation: on the one hand, they are part of a relatively large metal surface, and on the other hand, they are rapidly dissolved by reactive elements that decolorize and oxidize the silver metal.

One of the major problems with silver processes is the danger of leaving residual elements of iron (III) in the print, which oxidizes the silver particles and leads to image degradation.

Iron-silver processes use, without exception, the most common metal salt, silver nitrate. Nitrate is an oxidizing anion that tends to dissolve the colloidal image during wet processing, especially in an acidic environment.

A relatively more stable iron-silver process was the Satista process, which contained silver and also platinum.

1 – The Satista Process

In 1913, William Willis[28] of the British Platinotype Company patented the Satista process, the aim of which was to bring to market a less expensive process whose appearance would be very similar to that of platinum paper.

In the United States, Satista papers were distributed by the Willis-Clements Company in Philadelphia. Like the Platinotype papers, they were available in different surface structures, in sepia or black tones.

Satista paper was commercially available until the 1930s, but with the advent of Palladiotype paper, its decline began as early as 1916-17.

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[28] British Patent n° 20022, 4 sept.1913 - Brevet Français n° 462849, 22 sept. 1913.

James Thomson[29] published the following Satista formulae:

Pt Solution

potassium chloroplatinite	1,0 g.
orthophosphoric acid @ 20%	6,5 ml
eau, qswater, to make	65 ml

Sensitizing solution

iron oxalate (20%)	5 ml
water	20 ml
ferric ammonium citrate (green)	1,0 g
potassium oxalate	1,0 g.
Pt solution	0,5 ml
potassium dichromate (5%)	0,05 to 0,5 ml
arabic gum	0,5g.

Let stand for 24 hours before use.

Developer

water	48 ml
silver nitrate	4,0 g.
citric acid	1,0 g.
oxalic acid	1,0 g.

Working solution: 1+7. Storage and working solutions should be kept in brown bottles and in the dark.

Process for at least 1 minute. Rinse under running water for 2 minutes. Fix in a 4 % sodium thiosulphate solution. Rinse and dry[30].

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[29] THOMSON, James - A Silver-Platinum Printing Paper. In: American Photography, nov. 1915

[30] SMITH - Satista Paper. In: British Journal of Photography, vol.60, 1914.

2 – Contemporary Satista process, by Marek Matusz[31]

The process described differs in some details from the process published by Willis in "Sensitive Photographic Paper and Process of Making the same".

Sensitizing solution

Ammonium ferric oxalate (afo) in 25-40 % solution + Pt standard solution, i.e. K2PtC14 at 20 %. In its most concentrated form (40 %), the sensitizing solution crystallizes on different papers.

A standard formula for a 8x10 inch print:
1 drop of Pt solution
25 to 30 drops of afo solution

The process

Mr. Matusz extends the sensitizing solution with a glass rod for small sizes, and from 8x10 inches onwards with a Hake brush.

The amount of platinum is not very critical: more platinum gives black tones; less platinum gives browner colours. Palladium can also be used instead of platinum.

To obtain consistent results, it is necessary to dry thoroughly. For best results, the paper must be absolutely dry. In this form, sensitized paper can be stored for a few weeks.
Exposure is relatively fast: typical exposure time is 2 to 6 minutes. This is not a printing-out process, so test strips should be used.

The development is carried out with a 4% silver nitrate solution. The silver nitrate solution can be stored indefinitely in a brown bottle.

The development method is identical to the sensitization method. The exposed sheet of paper is fixed on a glass plate which is placed in an empty developing tray.

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[31] Article on www.alternativephotography.com/satista-prints/

Approximately 4 ml of silver solution is dripped onto the edge of the paper and a glass rod is used to spread relatively quickly and in a single pass the solution over the entire image surface . Some types of paper, however, can withstand several passes.

Remember that an excess of developer is required to prevent uneven development. For large formats, it is advisable to soak the exposed sheet of paper in the silver nitrate bath.

Allow the developer to work for about 2 minutes, then rinse under running water until the milky release of unexposed silver nitrate ceases; this takes about 5 minutes.

Clarification is carried out in a 4% tetrasodium EDTA solution or in a mixture of 2% EDTA and 2% citric acid.

After this, a gold, Pt or Pd toning can be carried out. The residual silver salt is removed in a fixing bath of 10% sodium thiosulphate.

After fixing for about 5 minutes, the finished print is rinsed under running water for about 30 minutes. Drying takes place in the open air.

3 – Contemporary Satista - process as per R. Sullivan

Due to the significant increase in Pt and Pd prices during 2000, the American Richard Sullivan developed an easy-to-use Satista process. It is based on studies by Stieglitz and Keiley on the development of platinum glycerine paper.

Oxalate solution

Ferric ammonium oxalate	10 g
Water	25 ml

Sensitizing solution

Oxalate solution	25 drops
Pt (or Pd) standard solution #3	3 drops

A drop of 1% or 2% ammonium dichromate solution may be added to increase contrast.

The sensitizing solution is spread with a Hake brush or glass rod.

The sensitive emulsion is dried thoroughly before being exposed by contact. The exposed paper is attached to a glass plate with adhesive tape.

Developer

Glycerin	10 ml
10% silver nitrate solution	2 ml

At this stage, the contrast can be increased by adding small amounts of ammonium dichromate.

The developer is spread using a brush or glass rod. Development is relatively slow and can take up to 5 minutes.

The print is completely darkened and can be cleared by rinsing in running water. Fixing is done in a weak 0.5% sodium thiosulphate solution.

Clarification is done in EDTA as in the Pt-Pd process. Final rinsing with running water. Air drying.

4 – Identification and conservation issues with Satista paper

According to the specialized literature, Satista and platinum prints were visually identical at the time of their creation. Historic Satista prints, however, show striking damage.

A recent study[32] highlights the types of damage identified: fading, yellow-orange color change, discolored fingerprints, and changes in image tonality.

The identification of Satista prints, damaged or undamaged, is made more difficult by their visual similarity to platinum-toned silver prints, such as callitypes toned in this way.

Even with X-ray fluorescence spectrometry (XRF), 100% identification is not possible. XRF shows traces of silver, platinum and sulphur (the latter as an aggressive element), all three of which can be present in both a Satista print and a platinum-toned callitype.

This seems to support the thesis that some platinum-silver prints in historical photo collections are mistaken for pure platinum prints.

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[32] Lisa BARRO - The Deterioration of Paul Strand's Silver-Platinum Prints. In: Abstracts Annual Meeting Photographic Materials Group of A.I.C., Puerto Rico, 2003.

XI – Pt-Pd toned silver gelatin prints

From the very beginning of photography, the unprotected silver print has been subject to degradation phenomena. Very quickly, a gold-toning process was developed to protect the silver particles in the emulsion. Later, Pt, Pd and selenium toning formulae were also used.

Platinum toning, which has only been used regularly since the 1890s, changes the tones of a photolytic silver image to brown. Platinum toning was generally used in combination with gold toning[33]; this gave more neutral tones and made the photographic emulsion more resistant to the oxidation of silver in the image.

Platinum toning

Distilled water	900 ml
Potassium chloroplatinite	0.5 g

Or

Potassium chloroplatinite (20% sol.)	2,5 to 3 ml
Citric acid	5 g
Sodium chloride (cooking salt)	5 g
Water, to make	1 000 ml

Palladium toning

Distilled water	900 ml
Sodium chloropalladite (15% sol.)	5 ml
Citric acid	5 g
Sodium chloride	5 g
Water, to make	1 000 ml

Gold chloride toning

Gold chloride (0.2% sol.)	50 ml
Ammonium thiocyanate (2% sol.)	50 ml
Water, to make	1 000 ml

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[33] Sylke HEYLEN - Onderzoeksraport i.v.m. chemische omkleuring van fotografische emulsies. Hogeschool Antwerpen, Optie C/R fotografie, 1996-97.

Toning procedure for printing-out emulsions

For processes such as salted paper, callitypes and silver chloride paper, the toning takes place before the fixing bath and after the water rinse removing the excess silver nitrate.

In general, the toning is carried out using the specified formulas, for 5 to 10 minutes under gentle agitation. When the desired tone is obtained, the print is washed for about 10 minutes.

The image is then fixed in a 10% sodium thiosulphate solution for 10 minutes or 2x5 minutes in two successive fixing baths. The print fades noticeably during fixing.

To minimize this fading, the fixing bath can be made alkaline by adding 2 to 3 g of sodium carbonate or bicarbonate per litre of fixing bath.

After fixing, an auxiliary rinsing bath with 1% sodium sulphite is used for 3 to 5 minutes with stirring, followed by a final wash. As it dries, the print darkens to its final tone.

A fractional gold-platinum or gold-palladium toning can be achieved by a partial toning in a gold chloride bath followed, after rinsing with water for 2 to 3 minutes, by a platinum (palladium) toning until the desired result is achieved.

XII – Multiple exposures on Platinum-Palladium prints

In the history of platinum printing, it was not uncommon to create superimposed prints, sometimes adding another technique to that of platinum. "Gum on Platinum" was a technique of choice for Alfred Stieglitz and Edward Steichen. Cyanotype and Van Dyke Brown were, and still are, used as overprinting techniques. This overprinting can be done simply or in register, taking care to exactly match consecutive identical images.

1 – Gum over Platinum

With this technique[34] , a finished Pt-Pd print is covered with a sensitive layer of gum arabic, which is then re-exposed and developed. This is adding a glossy layer to the Pt-Pd, creating more depth in the image and controlling the tonal values through the pigments included in the gum. It goes without saying that the platinum printer must also be familiar with gum printing.

Gum printing is a contact printing process in which gum arabic, watercolours and a photosensitive dichromate are combined to form an image.

The gum solution

Gum arabic	40g
Distilled water	100ml

The finely grounded gum is put in a bag and suspended in a glass of water for a few days. After dissolving, the pouch is squeezed and the gum is also filtered. The preservative-free gum solution can be stored for several weeks. The shelf life is extended by adding 10 drops of a 0.25% sodium benzoate solution. This must be dissolved in alcohol.

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[34] The procedure described here is the one used by René Smets, a belgian artist-photographer and inventor.

Gum arabic-pigment proportion

With gum printing, if the ratio between gum arabic (GA) and pigment is not correct, you risk getting unclean whites. The pigment in the whites should disappear completely during development. Three factors must be taken into consideration:

- the dilution of the GA solution: the more concentrated the gum solution is, the more pigment can be dissolved in the solution, but a thicker gum solution is more difficult to spread and tends to peel off during development;

- the type of pigment: when using pigments with low covering power and in too high a ratio to the GA solution, the whites will be stained;

- the paper and the sizing; the very structure of the paper may retain some of the pigments; this can be reduced by good beforehand sizing.

In order to control all the above data, a test can be carried out for each pigment and for each type of paper.

The test consists of making a series of dots with a different GA-pigment proportion each time, but without dichromate.
A certain amount of pigment is taken, e.g. 1 gram (or 3 cm out of a tube). For example, 8 ml of the GA solution is added. Mix everything well and, with a brush, make a patch (of a few cm) on the glued paper. Note the ratio, e.g. 1/8 (= 1 g pigment / 8ml GA) next to this stain.

Add 2 ml of GA to the mixture already made and make another patch on the paper, next to the previous one. Note the 1/10 ratio.

Repeat until a total of 26 ml GA (ratio 1/26) is reached. As far as possible, the same amount of emulsion is applied to the paper each time. After complete drying, the paper is allowed to float on a water bath (20°C) with the patched side down.

After about 30 minutes, remove the paper from the water and examine the patches. The last one that is completely dissolved in water (i.e. the one just before the stain that is still a bit visible) gives the right GA-pigment ratio for this pigment/paper combination.

Light sensitive emulsion

Potassium dichromate	10 g
Distilled water	100 ml
Ammonia 0,96 %	2 ml

The solution can be stored for a long time in a brown bottle. A deposit may form because 10% is a saturated solution.

The gum mix

Almost any colour can be used with dichromated gum. Either pigment powder or watercolour in tubes can be used.

<u>Light values layer</u>

1 part of gum
4 parts of potassium dichromate
1 x pigment
with a relative exposure time of 10 minutes.

<u>Middle tones layer</u>

1 part of gum
3 parts of potassium dichromate
2 x pigment
with a relative exposure time of 9 minutes

<u>Couche des ombres</u>

1 part of gum
2 parts of potassium dichromate
3 x pigment
with a relative exposure time of 8 minutes

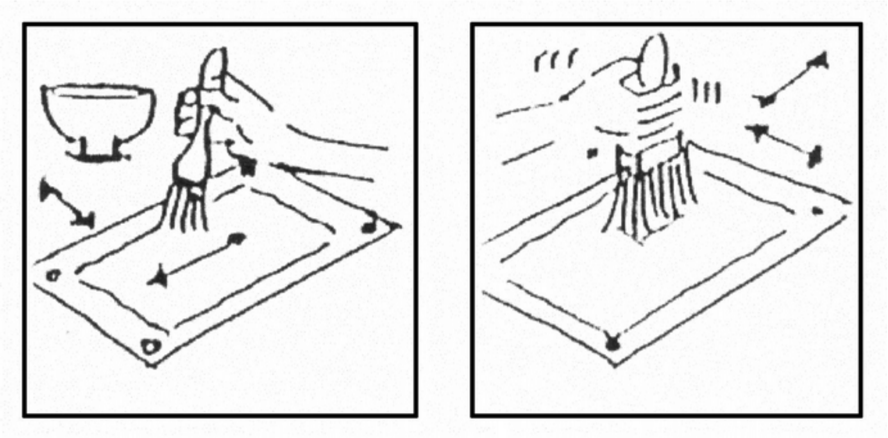
The exposure time under a UV-rich light source should be determined experimentally.

The required amount of gum is placed in a bowl using an eyedropper. The necessary powder pigment is then added. Instead of powder pigment, water-based paint in tubes can also be used.

Mix the gum and powder well with the brush. The gum must absorb the powder pigment completely until it forms a coloured liquid. Then add the quantity of dichromate and mix again.

Applying the gum layer

Use the spreading brush to take some gum solution from the bowl and spread it evenly over the paper. Spread the gum in all directions and make sure the entire image size on the paper is covered . Next, take the equalizing brush and even out the layer in all directions. Continue smoothing until the layer becomes more matte and slightly sticky.



Good coverage is achieved when the pencil marks indicating the boundaries of the image can still be clearly distinguished through the coloured layer. Now let the paper dry completely. After drying, the paper can be slightly moistened on the back and flattened between two blotters, under weight or in the press.

Exposure

Daylight or UV-rich tubes/lamps can be used for exposure. The exposure time is determined using test strips. Exposure is carried out until an image is clearly visible in the sensitive layer.

Development

A container is filled with cold water and the exposed paper is slid into it with the image facing upwards. When the paper has relaxed (about 2 minutes), turn the sheet over, making sure there are no air bubbles underneath.

Leave the image in water for +/- 30 minutes; the water is replenished several times, as soon as it is colored orange by the dichromate.

Remove the paper from the water, taking care not to damage the emulsion, and stick it against a slanted glass plate.

Carefully remove the unhardened pigmented gum with a plant sprayer or a sprinkler head on the water line. When no more dye is released, the image is fully developed.

Now the paper is dried again and, if necessary, a second layer of gum is applied for the medium tones. This is followed by: drying - exposure - development - drying. Finally, the third layer for shadows is applied in the same way.

Clearing the gum print

This is necessary because the potassium dichromate has slightly tinted the paper in orange.

Potassium disulphite	50g
Water	1liter

Then rinse with water for about 5 minutes, after which the final result can be dried.

2 – Cyanotype over/under Pt - Pd

As a contact process with a monolayer structure containing no silver, cyanotype printing can easily be combined with platinum and/or palladium printing without additional sizing.

The colour of the cyanotype is permanent. Berlin Blue, from which the cyanotype image is formed, is obtained by a chemical reaction and is therefore not a dye. It should be noted that cyanotypes do fear an alkaline environment. The use of alkaline paper should therefore be avoided at all stages of the process, from sensitization to image protection in a folder or mat of acid-free paper.

When exposed to light, the image can fade quite quickly. However, much of the density lost in this way can be recovered by storing it in total darkness.

The emulsion

The emulsion consists of two stock solutions that can be kept indefinitely as long as they are not mixed. Once mixed, the solution remains photosensitive for about three days, also when applied to paper. After that, the emulsion loses its sensitivity.

Solution 1:

• ferric ammonium citrate (green)	20 g
• distilled water	100 ml

Solution 2:

• potassium ferricyanide	8 g
• distilled water	100 ml

Both solutions are kept in dark, tightly closed bottles. Prior to use, equal parts of both are mixed together.

There are two kinds of ferric ammonium citrate: a brown and a green one, the green being the most sensitive. Ferricyanide forms the colour. Excess ferricyanide reduces the sensitivity of the solution to light. Too little ferricyanide can cause irregular tones.

Sensitization of the substrate can be carried out under 40W tungsten light; the emulsion is coated with a large soft brush (without metal parts) or the paper is floated for 2-3 min. on the sensitizing solution.

The coating is done with crossed brush strokes. The emulsion is light yellow-green in colour. If blue stains already appear during spreading and drying, the emulsion has been contaminated by metal, finger contact or a chemically unstable type of paper.

Drying

Drying takes place in total darkness. An indirect hot air flow, e.g. a hair dryer at a distance of one meter, accelerates the drying process and has no influence on sensitivity. The sensitized paper remains usable for about three days with a slight loss of sensitivity.

Exposure

Cyanotype paper is a low-sensitivity P.O.P. paper. It is necessary to overexpose because the highlights, when rinsed with water, fade noticeably. Exposure will therefore be continued until the light tones are significantly heavier than desired. It is advisable to calibrate the printing process using a grey wedge and densitometer readings.

Washing

The cyanotype is washed in running water at about 20°C for about 5 to 30 minutes depending on the thickness of the paper support. In case of insufficient washing, soluble iron salts remain in the image. Under the action of light, these will cause discoloration of the image. Rinsing in alkaline water for too long will also cause the image to fade.

Oxidizing bath

This stage is not absolutely necessary because the image will oxidize during drying. Its advantage: when it is carried out, the final blue colour of the image is formed immediately.
After washing, the cyanotype is placed in the next solution for a few seconds:

Water at 20°C ……………………………………….	200 ml
Hydrogen peroxide, 3% sol. ………………………..	20 ml

The cyanotype is then rinsed in running water and dried naturally in air or in a flow of pulsed hot air.

Contrast control

Image contrast can be increased by adding potassium dichromate to the photosensitive solution. Six drops of a 1% potassium dichromate solution per 2 ml of photosensitive emulsion gives a contrast increase of about 0.5 density units.

3 – Callitype over Pt - Pd

All variants of the callitype process, including the Van Dyke Brown process, can be used over platinum and/or palladium prints.

The only downside is the long-term image stability. These processes contain silver metal which, like the Satista process and the PT-Pd toning of silver emulsions, are subject to degradation by atmospheric sulphur.

Photosensitive solution

A.
Iron(III) ammonium citrate, 30% solution (storage solution)
B.
Tartaric acid, 5% solution (to be prepared immediately before use)
C.
Silver nitrate, 12.5% solution (storage solution)

Mix an equal amount (e.g., 20 ml) of solutions A and B; add an equal amount (20 ml) of solution C, drop by drop.
The light-sensitive solution is applied with a flat brush or a rod to the chosen substrate.

Air dry in total darkness.

Development

After exposure, wash in water at 20°C for 30 min. Treat for 3 min. in a 0.4% ammonium citrate bath.

Acidic gold chloride toning bath

Storage Solution A

Ammonium thiocyanate	5 g
Distilles water (50°C)	250ml

(leave it for 24 hours before use.)

Storage Solution B

Gold chloride, 1% sol.	50 ml
Distilles water	200 ml

Working solution

50 ml solution A
50 ml solution B
in 900 ml water

Tone for 3 to 10 min.

Fixing bath

Sodium thiosulphate, 2,5% solution
Fix for 3 to 5 min.

Auxiliary fixing bath

Kodak Hypo Clear Solution or 1% sodium sulphite solution.
Process for 3 to 6 min.

Washing and drying

As usual.

XIII – General information on P.O.P. Processes.

Exposure for Printing-Out Processes

The paper is generally very sensitive to fingerprints and should only be handled at the edges .

The negative is placed in intimate contact with the paper in a printing frame, vacuum or not. For large formats, there is a risk that the contact is not optimally ensured over the entire surface.

To guarantee the best possible result, care should be taken to use glass, which is less flexible than Plexiglas, and to increase the pressure exerted on the negative-support sandwich by adding a layer of foam rubber between the paper and the back of the printing frame.

P.O.P. emulsions are sensitive to blue, indigo, violet and ultraviolet light, and insensitive to green, yellow, orange and red light. Before and after exposure, the paper can be processed under low incandescent light. Fluorescent light causes fogging.

A blue and ultraviolet light source is used for exposure. Depending on the geographical location, exposure to direct or indirect sunlight is theoretically possible.

Reliable and relatively constant UV light is obtained by an array of BL (Black Light) type fluorescent tubes, or by a set of fluorescent tubes used for sunbeds. The number and length of the tubes is determined by the desired print size.

Under an array of BL or fluorescent tubes, at a distance of 10 to 15 cm from the printing frame, the exposure time varies from 3 to 10 minutes depending on the density of the negative. Other factors can influence the exposure time, such as the temperature and the composition of the developer.

All P.O.P. (Printing Out Papers) processes, which are direct blackening processes, produce a more or less contrasting image after the exposure phase. A conventional printing frame with a folding back allows the image formed during the exposure to be evaluated. Here, experience is the best advisor. Below we describe a technique for determining the exposure time using a grey scale.

It is still possible to burn or dodge parts of the image during exposure. Because of the enormous range of densities allowed by this technique, these manipulations are rarely used.

Calibration of the P.O.P. density range in function of the basic exposure time

It is important to obtain the darkest possible colour homogeneity of the paper and to ensure its reproducibility, sheet after sheet.

Using a gray scale with constant density steps (for example the Kodak Step #2 scale, or those fromf Stouffer or Agfatrans 25/125mm), we will determine the density range, as a function of exposure time, by applying elementary sensitometric rules.

There are two types of exposure devices:

- devices where the distance between the light source and the paper is fixed;
- devices where this distance can be controlled.

For the latter type, it is necessary to determine the distance at which an exposure of e.g. 5 min. produces a grey scale image in which the first two steps have equivalent density (blackening).

For non-height-adjustable exposure sources, the time (t) in seconds to reach the density described above should be noted.

It is also important to standardize the processing method.

The print is fully processed, carefully rinsed and air-dried to ensure its stability and preservation.

Using the Pt-Pd grey scale obtained, it is then possible to determine the characteristic curve of the paper. For this purpose, however, a reflection densitometer is required.

We know that the density of negatives is measured by transmission or transparency, and the density of prints by reflection. We also know that these values are presented on a logarithmic scale.

Each log of 0.3 corresponds to an area, with two grey scale steps, with a difference of 50% or 100% from the comparative density value.

We calculate the density corresponding to 90% of the maximum black value obtained with our exposure device and processing method.

The proposed graph contains a scale which allows, depending on variable density values, for example for shadows, to estimate the exposure time that causes a dark grey value of D=90 % in our print.

You then just have to read the exposure time corresponding to the density value chosen on the DNEG scale. Once again we would like to emphasize the approximate nature of this method of determining the exposure time, which should in fact be used as a shortcut and not as a method that guarantees a final result when choosing the ideal exposure for the final print.

It is well known that an increase of 0.3 density units over the reference density doubles the exposure time.

A reduction of 0.3 density units halves the exposure time.

The density values of the grey scale print described above have to be determined accurately. This is made possible by using an optical reflection densitometer.

The positive gray scale, once calibrated, can then also be used to compare other gray scale values from a processed and completely dried test strip .

Density Calibration when Making Enlarged Negatives

"Normal" negatives intended for silver gelatin prints on fiber base paper generally have a range of densities equivalent to a maximum of 6 grey scale levels.

A negative intended to be printed on Pt-Pd paper, for example, may contain about twice as many levels.

To extend the density range of a normal negative by making a duplicate copy, a halftone film such as Bergger BPFB-18 film is used. Such film can be processed in a normal paper developer.

The intermediate interpositive should contain all the shades of gray of the original negative, but with relatively low contrast.

This means that the dark parts of the enlarged positive film (shadows, black hair, ...) should have a density of D=1.0 to 1.3 and the detailed highlights a density of D=0.1 to 0.25.

For this purpose, the exposure time of the BPFB-18 emulsion must be adjusted to obtain these detailed highlights while the development time of the paper developer, e.g. Agfa Neutol developer, diluted to 1+10, must be adjusted to obtain low contrast shadows.

Next, the same technique will be used to obtain a more contrasted internegative by contact. The paper developer used will be diluted with water up to 1+3.

The exposure time of the internegative is chosen so that the density values D=1.0 to 1.3 of the above-mentioned interpositive will give density values of D=0.1 to 0.2 on the negative.

If it is then necessary to increase the development time in order to ensure a density range of D=1.8 to 2.0 in the highlights, it should be noted that the shadow density values increase relatively little and do not exceed the density D=0.45.

The best and quickest way to master this technique is to print, either by contact or by enlargement, the negative of a grey scale on the BPFB-18 emulsion.

In this way it is possible to calibrate very precisely the "ideal" negative, whose density range has been found by printing the reference scale.

The control of the obtained densities is preferably done by means of a transmission densitometer or, failing that, by visual comparison with the grey scale levels.

XIV – References

ABNEY, Captain - Platinotype, Its Preparation and Manipulation. Sampson, Marston Co, London, 1895.

ANCHELL, Stephen - The Darkroom Cookbook. Focal Press, Boston, 1994.

ANDERSON, Paul, L. - Pictorial Photography: Its Principles and Practice. Lippincot, Philadelphia, 1917.

ANDERSON, Paul, L. - Hand Sensitized Palladium Paper. In: American Photography, vol.32, july 1938.

ANON. - Comment on prépare soi-même le papier au platine. In: Bulletin de l'Association Belge de Photographie (ABP),vol. XXII, 1895.

ARBUTHNOT, Malcolm - Le procédé "gomme-platine". In: Bulletin de ABP, 1910.

ARENTZ, Dick - An Outline for Platinum-Palladium Printing, second edition, Flagstaff, Arizona, edition 1998.

ARNOW, Jan - Handbook of Alternative Photographic Processes. Van Nostrand Reinhold Co, N.Y., 1982.

BAKER, T. - Photographic Emulsion Technique. American Photographic Co, Boston, 1948.

BARGER, Susan, M. - Bibliography of Photographic Processes in Use Before 1880. The Graphic Arts Research Center, RIT, Rochester, 1980.

BARNIER, John — Coming into Focus. Chronicle Books, San Francisco, 2000.

BOSTICK & SULLIVAN - A Descriptive Catalog of Platinum and Palladium Chemicals and Related Products. Van Nuys, CA, 1987.

BOSTICK & SULLIVAN - Catalog of Materials Used in the Production of Hand Coated Platinum Photographs. Van Nuys, CA, 1992.

BOSTICK & SULLIVAN - LUMEN I to VI. Van Nuys, CA, 1982 to 1989.

BOSTICK & SULLIVAN - Ziatype: A Bostick & Sullivan Research Product. New Mexico, nd

BOVIS, Marcel - La papier à l'aniline et le papier au platine. In: Photo Ciné Revue, mai 1972.

BOVIS, Marcel & CHRIST, Yvan - 150 ans de photographie française. Editions de Francia, 1979.

BROWN, G.E. - Ferric and Heliographic Processes. Dawbarn & Ward, London, 1902.

BUNNELL, Peter - Non-Silver Printing Processes. Arno Press, N.Y., 1973.

BURBANK, W.H. - Photographic Printing Methods. Scovil & Adams Co, N.Y., 1891.

BURKHOLDER, Dan - Making Digital Negatives for Contact Printing. Bladed Iris Press, San Antonio Texas, 1998.

BURNETT, C.J. - On Printing by the Salts of the Uranic and Ferric Oxides. In: The Photographic Fine Arts Journal, vol.XI, n°VII, 1858.

CLARK, Lionel - Platinum Toning. W. & H.T. Anthony, London, 1890.

CLERC, L. P. - La technique photographique, Editions P. Montel, Paris, 1934.

COE, Brian - Techniques of the World's Great Photographers. Chartwell Books, Inc., New Jersey, 1981.

COE, B. & HAYWORTH - BOOTH, M. - A Guide to Early Photographic Processes, Victoria & Albert Museum, London, 1983.

COLLET, Jacques - Procédé au platine-palladium. Notes de stage, Paris, 1992.

COTTINGTON, lan E. - Platinum and Early Photography: Some Aspects of The Platinotype. In: History of Photography, vol.10, n°2, 1986.

CRANE Tillman — Making Enlarged Negatives. In : View Camera Magazine, sept./oct. 1992.

CRAWFORD, Wiliam. - The Keepers of Light. Morgan & Morgan, N.Y., 1979.

CURTIN, Barbara - Out of the Blue. In: Professional Photographer, 32, 11, 1992.

DAVIS, Phil. - Beyond the Zone System. Van Nostrand Reinhold, N.Y., 1981.

DAWSON, George - The Platinotype Printing Process. In: British Journal of Photography, vol.27, n°1029, 1880.

DE HAAN, Gerretje, G. - Cyanotypie, recycling the blues. In: Edele Procédés, Professionele Fotografie Special, n.d.

DE PAULA CEMBRANO, F. - Impressions au sels de platine. In: Bulletin de l'ABP. vol.XVI, 1889.

EATON, George - Photographic Chemistry, Morgan and Morgan, Dobbs Ferry, NY, 1999.

EDER, J.M. - Die Lichtpausverfahren, die Platinotypie und verschiedene Kopierverfahren ohne Silbersalze. Wilhelm Knapp Halle, 1929

FARBER, Richard - Historic Photographic Processes. Allworth Press, New York, 1998.

FRAPIE Frank R. & WOODBURY, Walter E. - Photographic Amusements : Including Tricks and Unusual or Novel Effects Obtainable with the Camera. American Photographic Publishing, Boston, 1931.

GANICHOT, P. - Sur un nouveau procédé de platinotypie. In: Bulletin de ABP, vol. XIX, 1892.

GASSAN, Arnold - Handbook for Contemporary Photography. Light Impressions, Rochester, 1977.

GENT, Megan - Prints and Permanence: A Review of 19th Century Photographic Processes with Particular Regard to the Chemical Stability of the Image. Essay. Royal College of Art. V&A, London, 1992

GENT, Megan - An Investigation of a Practical Treatment for Removing Iron Stains in Platinum Prints. Final Year Project. Royal College of Art, V&A, London, 1993.

GENT, Megan & Rees Jacqueline - A Conservation Treatment to Remove Residual Iron from Platinum Prints. In: The PaperConservator, 1994.

GLAFKIDES, P. - Chimie et physique photographique. P. Montel, Paris, 1976.

GLINSMAN, L. & McCABE, C. - Understanding Alfred Stieglitz's Platinum and Palladium Prints: Examination by X-Ray Fluorescence Spectrometry. In: Conservation Research, vol.51, Monograph Series II, National Gallery of Art, Washington DC, 1995.

GOODMAN Allan - Elegant Images. Instructions and Trouble-shooting Guide for Platinum and Palladium Photoprinting. Elegant Images, Delaware, 1976.

GOTTLIEB, Adam. - Chemistry and Conservation of Platinum and Palladium Photographs. In: Journal of the American Institute for Conservation, vol.34, n°1, 1995.

GOTTLIEB, Adam. - Senior Thesis, Princeton University, 1993.

GOURMAND, M. - La restauration des photographies. Mémoire de diplôme, Institut Francais de Restauration des Œuvres d'Art, IFROA, Paris, 1987.

HAFEY, John & SHILLEA, Tom - The Platinum Print. The Graphic Arts Research center, Rochester, 1979.

HAHN Betty - Photography or Maybe Not. University of New Mexico Press, Albuquerque, NM, 1995.

HALL Henry - The Kallitype Process. The Photo Miniature, vol.IV, n°47, 1903.

HAMMOND John - The Camera Obscura: A Chronicle. Adam Hilger Ltd, Bristol, England, 1981.

HANSCH, M. - Frühe Photographiën: Ihre Technik and Restaurierung. Kabinet Verlag, Uwe Scheid, 1985.

HARRISON, G. - Les différents procédés au platine. In: Bulletin de 1'ABP, vol.XVII, 1890.

HENDRIKS, K. et al. - The Duplication of Historical B&W Negatives. In: Journal of Imaging Technology, vol.12, n°4, 1986.

HERSCHEL, J.F.W. - On the Action of the Rays of the Solar Spectrum on Vegetable Colours and on Some New Photographic Processes. Philosophical Transactions of the Royal Society, 1842.

HESS NORRIS, Debbie - Platinum Photographs: Deterioration and Preservation. In: Photographic Conservation, vol.7, n°2, 1985.

HEWITT Barbara - Blueprints of Fabric: Innovative Use for Cyanotype. Interweave Press, Loveland, CO, 1995.

HOFFMAN, M. - Notice sur le platinotype. In: Bulletin de l'ABP, vol.XVI, 1889.

HOLTZMAN H. — Alkali Resistance of the Iron Blues. Industrial and Engineering Chemistry, 37, 1945.

JACOBY, Richard. - Le fixage des épreuves au platine. In: Bulletin de l'ABP, vol. XXVIII, 1901

JAMES, Christopher - The Book of Alternative Photographic Processes. Delmar, Thomson Learning, Canada, 2002.

JONES, E. Bernard, Ed. - The Encyclopedia of Early Photography , Bishopgate Press, London, 1981.

KEILEY, J. - Une nouvelle méthode de développement pour le papier au platine. In: Bulletin de l'ABP, vol.XXVIII, 1901.

KINGSLEY, Hope - Workshop Notes on the Cyanotype Process. In: Silverprint Catalogue, London, 1993.

KOCKAERTS, Roger - Procédés nobles en photographie: Platine-Palladium, Cyanotypie, Editions pH7, Bruxelles, depuis 1994.

KOCKAERTS, Roger - Identificatie, technologie en c/r technieken van historische fotoprocédés. Deel 1: procédés gebaseerd op de lichtgevoeligheid van zilverzouten Ed. pH7, Brussel, 1994.

KOCKAERTS, Roger - Identificatie, technologie en c/r technieken van historische fotoprocedes. Deel 2: procedes gebaseerd op de lichtgevoeligheid ijzerzouten, Ed. pH7, Brussel, 1996.

KOCKAERTS, Roger - Identificatie, technologie en c/r technieken van historische fotoprocedes. Deel 3: procédés gebaseerd op de lichtgevoeligheid van chromaatzouten Ed. pH7, Brussel, 1996.

KOSAR, J. - Light Sensitive Systems. Wiley & Sons, N.Y., 1965.

LAVEDRINE, Bertrand - La conservation des photographies, Presses du CNRS, Paris, 1990.

LIESEGANG, Ed. - Virage aux sels de platine. In: Bulletin de l'ABP, vol. XXI, 1894.

LONDE, A. - Aide-mémoire pratique de photographie, Bailliere & fils, Paris, 1897.

MALDE Pradip — New Solutions for Platinum Printers. In : View Camera Magazine, sept./oct. 1992.

MARK, Gordon. - Coating Platinum Emulsion for Maximum Density. In: Lumen VI, Summer, 1989.

MASKELL, Alfred. - Conférence sur la platinotypie. In: Bulletin de l'ABP, vol.XIX, 1892.

MOOR, I. & A. - The Conservation of Anna Atkins' British Algae. The World's First Photographically Illustrated Work. ESHPh Symposium Vevey, 1989.

NADEAU, Luis - The History and Practice of Platinum Printing. Ateliers Nadeau, Fredericton, CND, 1984. - 2nd revised edition: 1991.

NADEAU, Luis - Encyclopedia of Printing, Photographic and Photomechanical Processes. Fredericton, CND, 1988.

NAUMANN, Felix. - Die Technik des Platindruckes. Liesegang, Leipzig, 1910.

NETTLES Bea - Breaking the Rules: A Photo Media Cookbook. Inky Press Productions, Rochester, NY, 1977. Expanded 3th edition: Urbana, Illinois, 1992.

NEWHALL, Beaumont. — The History of Photography, Museum of Modern Art, New York, 1982.

PARDOE, Don. - Reversal Process. In: Lumen IV, 1984.

PIZZIGHELLI, G. - Des épreuves au platine. In: Bulletin de l'ABP, vol.X, 1883.

PIZZIGHELLI, G. & HUBL, A. - Platinotypie. Harrison & Harrison, London, 1886.

PIZZIGHELLI, HUBL, HORSLEY, HINTON & EMERY. - Le procédé au platine. Editions Jean Michel Place, Paris, 1986.

POLLMEIER, K. - Der Platindruck. In: Profifoto, 1, 1992.

REED, Martin & JONES, Sarah - Silver Gelatin, Amphoto, New York, 1996.

REILLY, James - The Albumen & Salted Paper Book, Light Impressions, Rochester, New York, 1980.

REILLY, James - Care and Identification of 19th Century Photographic Prints. Eastman Kodak, Rochester, 1986.

RENNER, Eric & SPENCER, Nancy - Pinhole Photography, Focal Press, Stoneham, 1994.

REXER Lyle - Antiquarian Avant-Garde: The New Wave in Old Process Photography. Harry N. Abrams, New York, 2002.

REXROTH, Nancy - The Platinotype. Violet Press, Yellow Springs, 1977

RICE, Ted - Palladium Printing Made Easy. Eagle Eye Text Productions, Santa Fe, NM, 1994.

RICHARDSON, Carlos - Palladium Printing. In: Camera, Lucerne, 2, 1979.

ROMANO Clare, ROSS John & ROSS Tim - The Complete Printmaker. Collier Macmillan Publishers, New York, 1990.

RUDIAK John — Creating a Platinotype. In : View Camera Magazine, july/aug., 1994.

SCHAAF Larry — The Birth and Early Years of Potography. Royal Photographic Society, London, 1989.

SCHAAF Larry - Out of the Shadows : Herschel, Talbot and the Invention of Photography. Yale University Press, New Haven, CT, 1992.

SCHAAF Larry & KRAUS Hans - Sun Gardens : Victorian Photograms by Anna Atkins. Aperture, New York, 1985.

SCOPICK David - The Gum Bichromate Book, Light Impressions, Rochester, 1987.

SEIGEL Judy ed. - Post Factory Photography, Journal of Alternative and Non-Silver Processes. N°1 to 9, New York, 1998 to 2003.

SEVERSON, Douglas, G. - Alfred Stieglitz's Palladium Photographs and Their Treatment by Edward Steichen. In: Journal of the American Institute for Conservation, vol.34, n°1, 1995.

SHILLEA, Tom. - Instruction Manual for the Platinum Printing Process. RIT, Rochester, 1986.

SPILLER, M. - De la stabilité des épreuves aux sels de platine. In: Bulletin de l'ABP, vol.VII, 1880.

STEINBERG, Robert, J. - Palladio Instruction Manual. The Palladio Co, Inc., Cambridge, MA, 1991.

STEINBERG, Robert & Sura. - The Palladio Irregular, The Palladio Co, Cambridge, MA, vol. 1 to 3, 1990 to 1993.

STEVENS Dick - Making Kallitypes: A Definitive Guide. Butterworth & Heinemann, Stoneham, MA, 1990.

STIEGLITZ, A. & KEILEY, J. - Le procédé à la glycerine. In: Bulletin de l'ABP, vol. XXVII, 1900.

STIEGLITZ, A. & KEILEY, J. - The "Camera Notes" Improved Glycerine Process for the Development of Platinum Prints. In: Lumen VI, 1989.

SULLIVAN, R. - Labnotes. Bostick & Sullivan, Van Nuys, CA, 1982.

SULLIVAN Dick & WEESE Carl - The New Platinum Print. Working Pictures Pressbook, Santa Fe, NM, 1998.

TENNANT, John, A. - Platinotype Modifications. In: The Photo Miniature, vol.4, n°40, 1902.

TENNANT, John, A. - Platinum Printing. In: The Photo Miniature, vol.10, n°105, 1911.

TICE, George - Platinum Printing. In: Darkroom. Lustrum Press, N.Y., 1977.

TICE, George - In: Caring for Photographs. Life Library of Photography, 1972.

TODD Hollis & ZAKIA Richard — Photographic Sensitometry. Morgan & Morgan, Dobbs Ferry, NY, 1969.

VANDEKERKHOVE, Henk. - Historische fotografische procédés, Gent, 1988.

VANDERKINDERE, M. - Une variante du procédé au platine d'après Lewinsohn. In: Bulletin de l'ABP, 1910.

VANDERKINDERE, M. - Les différents traitements du papier au platine. In: Bulletin de l'ABP, 1911.

VAN KEUREN Sarah - A Non-Silver Manual, Self Published, University of the Arts in Philadelphia, 1999.

WADE Kent - Alternative Photographic Processes. Morgan & Morgan, Dobbs Ferry, NY, 1978.

WARE, M. J. - Platinum Reprinted. The British Journal of Photography, october 1986.

WARE, M. J. - An Investigation of Platinum and Palladium Printing. In: The Journal of Photographic Science, vol.34, 1986.

WARE, M. J. - The Argyrotype Process. In: The British Journal of Photography, vol.13, 1991.

WARE, M. J. - Cyanotype : The History, Science and Art of Photographic Printing in Prussian Blue. Science Museum and Museum of Photography, Film and Television. London, 1999.

WARREN, W. J. - The Platinotype Process of Photographic Printing. Iliffe Sons, London, 1899.

WEBB Randall & REED Martin - Spirits of Salts. Argentum, Aurum Press, London, 1999.

WEESE Carl - Ziatype : A Brand-New Nineteenth-Century Process. In : Photo techniques, vol. 18, n°4, 1997.

WEINSTEIN, Robert & BOOTH, Larry. - Collection,Use and Care of Historical Photographs. American Association for State and Local History, 1977.

WILLIS, W. - British Patents. n°2011 (1873), 2800 (1878), 1117 (1880), 1681 (1887), 16003 (1887), 20022 (1913).

WITKIN Lee & LONDON Barbara - The Photograph Collector's Guide, New York Graphics Society, Boston, 1979.

WYNNE Thomas - The Kallitype, Photographer's Formulary, Missoula, 1982.

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