

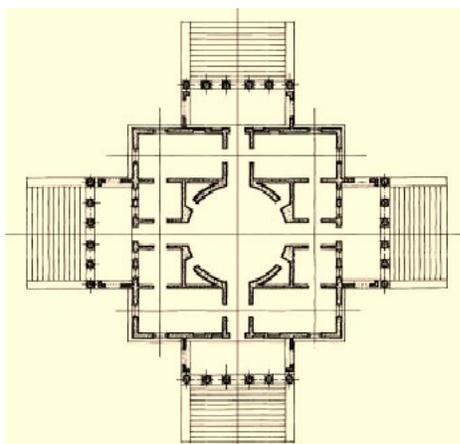
Platinomicon

A Technical Account of Photographic Printing in Platinum and Palladium

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Preface to the Platinomicon

This is a compilation of the history, practices, and underlying chemistry of the photographic printing processes in platinum and palladium metals. It has grown out of a report that was first commissioned in 2010 by the National Gallery of Art in Washington DC. My initial remit for that consultancy was to focus specifically on the outstanding body of artistic work in this medium due to Alfred Stieglitz, which is in the keeping of the Gallery. The original aims may be inferred from my *Preface to an Interim Report* of 2010, which follows. However, with the growing interest and contributions from many current researchers and conservators, the purposes of this study have expanded, broadening its scope to embrace the technical aspects of most of the historic printing in platinum and palladium, and including some contemporary practice.

This resulting text therefore represents an attempt to provide a fairly comprehensive handbook to the processes: it is intended for photohistorians, curators and conservators of photographs, photoscience, photographic print-makers, and for all the possible hybridizations of those disciplines. The first portion of this book is devoted to the history and practice, within which it strives to be readable without demanding any specialised knowledge of chemistry. The latter portion on conservation and chemistry does assume some familiarity with chemical principles and formulae, especially how they enable our understanding of the issues of print quality, stability, and deterioration. To clarify the technicalities, Appendix I attempts to explain the relevant chemical jargon and Appendix IX provides a glossary for the general reader. The other Appendices include: a chronology of the processes; a 'workflow' for making digital internegatives; preparative methods for some key chemicals; and complete transcripts of the six relevant patents by William Willis, the inventor of Platinotype and Palladiotype.

Over the years 2010–2015 at the National Gallery of Art, the Andrew W. Mellon Foundation has funded a major research project into the preparation and conservation of platinum and palladium prints; I join my colleagues at the Gallery in acknowledging our gratitude for this generous grant, without which this text would have been so much the poorer. A most welcome outcome of this research initiative has been a sharing of interests in the medium and its conservation across two dozen major institutions in the USA: museums, studios, galleries, libraries, archives and universities, involving some 46 conservators, curators, and museum scientists – the “Platinistas” – who presented the first fruits of their researches at an international symposium entitled *Platinum and Palladium Photographs: Technical and Aesthetic History, Chemistry, and Connoisseurship*, which was held in Washington DC in October 2014 under the aegis of the American Institute for Conservation of Historic and Artistic Works. The initiative for unifying this collaboration and driving it through to a major international conference and a subsequent publication can be directly attributed to the boundless enthusiasm, energy and dedication of the National Gallery's Head of Photograph Conservation, Constance McCabe, and her colleagues at the NGA, to whom I offer my warmest and most appreciative thanks.

Mike Ware, Buxton, 2016

1. Evolution of the Platinotype Process

Throughout most of human history, prior to the founding of chemical science about three centuries ago, the known metallic elements were only seven in number, namely: copper, silver, gold, mercury, tin, lead, and iron.¹ With these as our entire metallic resource, including their various alloys such as bronze and pewter, humankind learned how to fabricate metal tools and vessels, weapons, mechanisms, decorative jewellery and enduring art. Just two of these elements, silver and gold, were dignified by the alchemists as 'noble metals', owing to their resistance to being transformed by fire.

1.1 Discoveries of platinum and palladium

The seven metals of classical antiquity were eventually supplemented by a third noble metal, platinum – popularly called 'The Eighth Metal' – around 1748, when it was first made known in Europe. This discovery is usually attributed to the Spanish naval officer Don Antonio de Ulloa (1716–1795), who had been seconded on a French scientific expedition to Ecuador and Colombia, where the metal had long been recognised by the local inhabitants – and rejected as an 'impurity' – in the gold mines of the Chocó region.² However, there is evidence from a series of publications in the *Philosophical Transactions of the Royal Society* for 1749–50,³ that a sample of platinum had previously been brought to England in 1741 by the metallurgist and British Government assay-master, Charles Wood (1702–1774), who was stationed in Jamaica and came across the specimen there, where its source reputedly had been "Carthagenia in New Spain", *i.e.* the Spanish West Indies, now Colombia.⁴ This sample was eventually donated to the Royal Society in 1750 and its scientific investigation began.

The name 'platinum' derives from the Spanish diminutive *platina*, meaning 'little silver'. For many years platinum remained no more than a curiosity, and it only found use in the early 19th century for the fabrication of scientific apparatus and vessels; its extremely high melting point and 'nobility' – its unsurpassable resistance to chemical attack – made it a valuable material for containers, electrodes, weights, and measures to establish the experimental foundations of quantitative chemistry and physics. In 1847, John William Draper, see Appendix I, proposed a device utilising an incandescent platinum foil as a primary standard of luminous intensity, thus defining the first international unit for the brightness of light, the candela.⁵

The element palladium, the lighter congener of platinum, was not discovered until 1803, in platinum ores, by William Hyde Wollaston (1766–1828), the inventor of that subtle optical drawing-aid, the *camera lucida*.⁶ Although less dense than platinum, palladium still qualifies as a 'noble metal'. It is named after the Greek goddess of wisdom, *Pallas Athena*, and shares the name with *Pallas*, the second-largest of the asteroids, then newly-discovered by Wilhelm Olbers in 1802.⁷ The eponym 'palladium' derives directly from the classical Greek *παλλάδιον*, *Palladion*, the wooden statue of *Pallas Athena* that was regarded as a protective icon and a safeguard for the city of Troy. This fourth noble metal, when appropriately alloyed with other metals, soon found

use to make the calibrated scales of precision instruments, and for dentistry, jewellery, and in modern times as an important chemical catalyst.

1.2 Noble metals in photography

It is silver, thanks to the uniquely high light-sensitivity of some of its salts, that has always been the essential metal for photography, beginning with the first announcements of this innovation in January of 1839, when Louis Jacques Mandé Daguerre (1787–1851) and William Henry Fox Talbot (1800–1877), made public their respective, independent inventions of silver photography on metal surfaces and on paper. It soon transpired that both types of silver photograph could suffer from impermanence: silver metal, although noble, is particularly susceptible to sulphiding, with consequent fading of the image. Two other leading pioneers of photographic process, John Frederick William Herschel (1792–1871) and Robert Hunt (1807–1887), were also keenly aware of the vulnerability of silver images, and both recognised that the noble metal platinum was potentially an ideal substance to resist this problem. As a sign of his dissatisfaction with silver chloride as an imaging substance that could exhibit “capricious differences”, Herschel made the early comment:

“I was on the point of abandoning the use of silver in the enquiry altogether and having recourse to Gold or Platina.”

which comes from his paper of 1839 to the *Philosophical Transactions of the Royal Society*, the manuscript of which was withdrawn before publication but re-discovered in 1979 by the eminent photohistorian Dr. Larry J. Schaaf.⁸

Herschel’s reference here to “platina” recalls his own discovery in the ‘pre-photographic’ year of 1831, that a particular platinum salt solution was observed to be sensitive to light, forming a white precipitate of ‘platinate of lime’ when illuminated.⁹ Schaaf has drawn attention to this phenomenon as a significant forerunner to the invention of photography,¹⁰ although this photochemical aquation reaction does not actually lend itself to furnishing images on paper. While he was visiting Hamburg, Herschel became aware that the German chemist, Johann Wolfgang Döbereiner was pursuing parallel researches on the photosensitivity of iron salts. This discovery spurred Herschel to write on 12 June 1832 to his colleague Dr. Daubeny, who agreed to read Herschel’s paper on the photosensitivity of calcium platinic chloride solution, to the Oxford meeting of the British Association for the Advancement of Science on 22 June 1832, in order to establish his priority in this area of photochemistry, and to announce his intention of continuing with an analysis to identify the product. Herschel’s paper was subsequently published,¹¹ but was also translated and published in the German literature.¹² The German transcript carries a long editorial footnote (signed only ‘Br.’) referring to Döbereiner’s work, part of which can be translated from the German thus:

‘Following this communication from Döbereiner we further note that we have repeated Herschel’s experiment and found it to be confirmed...Thus a compound of platinum oxide with calcium oxide has been formed through the action of light. We have not made any analysis of this compound,

however, in order not to anticipate Herr Herschel, and content ourselves by confirming the facts.'

So Herschel's result was quickly confirmed in Germany by repeating the experiment, and acknowledged with a declaration that there was no intention of further trespassing in Herschel's field. Despite this disavowal, Döbereiner subsequently initiated and supervised a research project into the analysis of Herschel's 'platinate of lime', in order to determine a formula for the photoproduct, which Döbereiner published in 1835, during Herschel's astronomical sojourn in the Cape of Good Hope.¹³ While it was not in Herschel's nature to harbour resentment, it is possible that this action may have left him with a natural feeling of antipathy towards his rival in photochemistry that he expressed only by completely shunning and remaining silent thereafter on the subject of Döbereiner's work, (see §1.6).

There are several other precedents for the detection of a sensitivity to light in salts of various metals, especially iron, due to Count Bestuscheff (1725),¹⁴ Adolph Ferdinand Gehlen (1804),¹⁵ Henri August Vogel (1813),¹⁶ and Johann Wolfgang Döbereiner (1831) as mentioned above.¹⁷ While these observations were clearly nourishment for the embryonic sub-science of photochemistry, none of them can be said to feed directly into the conceptual history of the invention of the photographic process. For that, there must also be some intention on the part of the inventor to form or capture an image,¹⁸ such as was the case in the experiments of Johann Schulze (1725),¹⁹ possibly Elizabeth Fulham (1794),²⁰ and certainly Thomas Wedgwood (1799),²¹ and Nicéphore Niépce (1820s).²² But it was the truly photographic innovations with silver salts due, separately, to Talbot and Daguerre in the 1830s, and the possible use of platinum for photography,²³ that stimulated both Herschel and Hunt to devise attempts to make images in noble metals, as will be described next.

1.3 Sir John Herschel's siderotypes

In his paper on photography to the Royal Society in 1839, cited above in §1.2, among other possibilities Herschel retrospectively envisaged making images with a platinum salt sensitizer; the abstract of that paper, published in the *Athenaeum*, states that one of the most promising processes that presented themselves to him was:

"...the instant and copious precipitation of a mixture of a solution of muriate of platina and lime-water, by solar light, forming an insoluble compound, which might afterwards be blackened by a variety of agents..."²⁴

But there is no record that he actually made any images by this means, and nor has anyone else.²⁵ In his subsequent 1840 paper in the *Philosophical Transactions of the Royal Society*,²⁶ Herschel did report testing platinic chloride, which proved insensitive to light, and platinic iodide which, although light-sensitive, only yielded evanescent images – probably in iodine not platinum.

The breakthrough in noble metal photography came in 1842 as a result of Herschel's quest for a system of colour photography, when he turned to an iron salt, ammonium ferric citrate, that had been recommended to him by chemist-physician Dr. Alfred Smee (1818–1877). Herschel found it to be highly sensitive

to light, which transforms this ferric salt into a ferrous salt that can, in turn, react with potassium ferricyanide to form Prussian blue – ferric ferrocyanide – with which Herschel succeeded in making images that he called cyanotypes.²⁷ Herschel's quick chemical intuition suggested that this light-sensitive iron salt could also be used to reduce gold chloride to the metal, or silver nitrate to silver, or mercuric salts to mercury, all of which he successfully demonstrated, but he found that the same method did not work for platinic chloride.²⁸ So Herschel was able to use this iron salt, and the similar ammonium ferric tartrate, to make images in Prussian blue, gold, silver, and mercury, giving rise to the entirely novel photographic printing processes that he named respectively: cyanotype, chrysotype, argentotype, and kelaionotype.²⁹

All these were different examples of a new general class of photographic process based on light-sensitive salts of iron, which Herschel dubbed collectively as "siderotype", from the Greek for iron, σιδηρος (*sideros*). He first proposed this word in a modest footnote to a report in *The Philosophical Magazine* of the meeting of the Royal Society, gathered to hear his 1842 paper:

"Note by the Author.– A solution of silver produces a like effect, and with greater intensity, but much more slowly. Consequently the name Chrysotype would seem less appropriate than Siderotype.–J.F.W.H." ³⁰

Herschel's neologism was soon approved by the editor of *The Edinburgh Review*, the distinguished physicist, Sir David Brewster:

"Hence Sir J. Herschel considers the name *siderotype*, taken from the *iron* employed in one of the solutions, as preferable ..." ³¹

The name "siderotype" then entered the canon of scientific reference as a headword in Henry Watts' *Dictionary of Chemistry*, although the description there is somewhat restrictive, and misleadingly suggests its use in the camera, rather than by contact, which would have required exposures of many hours:

"SIDEROTYPE. A method of producing sun-pictures by means of ammonio-ferric citrate. Paper impregnated with this salt is exposed to light in the camera, and the picture is developed with a neutral solution of gold or, better, of silver. (Herschel, Phil. Mag. [3] xxi. 225.)" ³²

This word has proved to be a useful collective noun defining the whole class of iron-based photographic processes, which was later to include platinotype and palladiotype and several others (see Table 11.2 in §11.3).

Robert Hunt's monograph of 1844, *Researches on Light*, describes a rather complex platinum-containing sensitizer yielding prints on which he optimistically bestowed the misnomer of "platinotypes", but it is evident from their fading within a few days that these images could not have contained any platinum metal. They probably consisted of precipitated mercury, a salt of which was used in the developer, and the volatility of which was responsible for their fading, just like Herschel's kelaionotypes, to be described in §9.12.³³

1.4 Charles Burnett's experiments

The photographic experimentalist Charles John Burnett (1820–1907) of Edinburgh has been credited with making and exhibiting platinum prints as

early as 1859 at the meeting of the British Association for the Advancement of Science held in Aberdeen.³⁴ On the final day of the meeting, Wednesday 21st September, a newspaper report records that:

“Mr. C. J. Burnett showed some specimens illustrating the use of platinum in photography.”³⁵

However, this probably referred to the platinum toning of silver prints as described in §1.5; the evidence from Burnett’s publications reads rather inconclusively,³⁶ and there are no known specimens of his prints.³⁷ What is clear from his writings is that he must have successfully made and exhibited palladium prints around that time, so he deserves credit for anticipating Willis's Palladiotype process of 1917, albeit his photochemistry was not based on iron, but on a uranium(VI) salt being reduced to uranium(IV) under the action of light and in the presence of organic matter, such as the paper or its sizing agent. The uranium(IV) could in turn reduce a noble metal salt to the metal. Burnett's uranium printing processes were capable of yielding images in stable substances, just like the siderotypes. By this means, Burnett made the first palladium prints in 1856, and obtained fine images in gold and silver.³⁸

Burnett, however, admitted to a certain personal lack of patience and perseverance in his photographic researches:

“I cannot well find time for the prosecution of discovery, and for pretty specimen making, and as soon as I see unmistakable indications of what are the real capabilities of any process, I am generally off to something else.”³⁹

He was soon given cause to regret this capriciousness, when his priority was challenged by a cousin of the pioneer Nicéphore Niépce, the French photographic innovator, Abel Niépce de Saint Victor (1805–1870), who published and sought patent rights in 1858 for uranium printing processes essentially identical to those described by Burnett a year earlier.⁴⁰ Unsurprisingly, this gave rise to some highly acrimonious exchanges in the press of the day, with Burnett making justifiable accusations of:

“...most monstrous and systematic plagiarism.”

Burnett showed his *Experiments in Printing* at the London International Exhibitions in 1859 and 1862, and was commended with an 'Honourable Mention', but none of his prints is known to have survived. A similar uranium sensitizer was also later employed by Jacob Wothly in 1866 to make "feeble blue-black prints" in platinum and palladium, but these had to be intensified by toning in a bath of gold chloride, so the process went no further and died the same death as the egregious and unsuccessful 'Wothlytype' (patent 1864).⁴¹

1.5 Platinum toning of silver images

From the earliest days of photography, the toning of silver images with gold had been adopted as a means of ensuring their greater longevity and more acceptable appearance; the practice became standard, both for 'gilding' daguerreotypes and for improving the colour and stability of the albumen prints of later decades.⁴² The use of platinum instead of gold, as a toning and stabilising agent for silver prints, was much less common, and histories record

that it was first carried out by Ernest de Carranza in 1856, using a solution of platinic chloride.⁴³ However, evidence has been found recently from the studies of Dusan Stulik *et al* by X-ray fluorescence spectrometry that platinum toning of albumen silver prints was successfully accomplished a little earlier, in 1854, by Eugène Durieu (1800–1874).⁴⁴

This toning procedure was also taken up by C.J. Burnett during 1857–59, but it never came into general use because the process using platinic chloride tended to weaken the silver image:

“Mr Burnett exhibited [Photographic Society of Scotland] some photographs toned with a solution of bichloride of platinum, the objections to the use of which he had attempted to remove to a certain extent by the addition of carbonate of soda.”⁴⁵

Platinum toning of silver prints would not become fully practicable until after the invention of platinum printing itself, for chemical reasons that will become apparent in the next section, and are fully described in Lyonel Clark's monograph of 1890 on *Platinum Toning*.⁴⁶

1.6 William Willis's invention

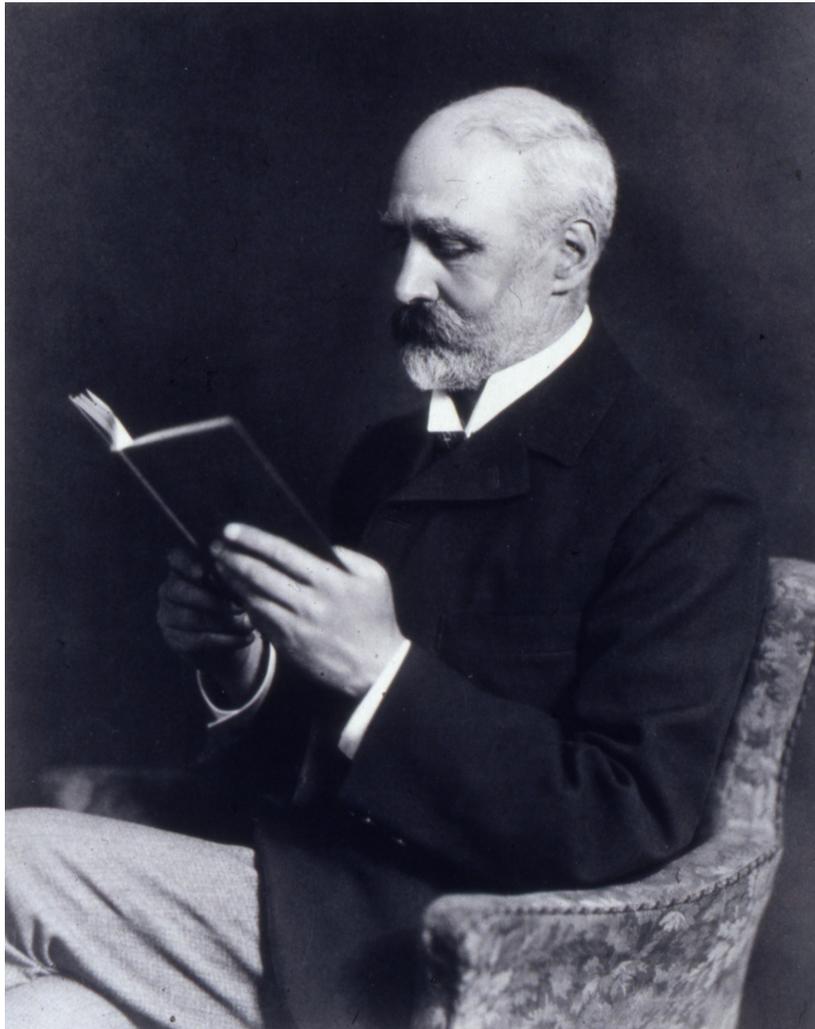


Fig. 1.1 William Willis, Junior (Platinotype print by an unknown photographer)

Despite the best endeavours of the pioneers of photography, the goal of making prints in pure platinum did not show any real promise of being achievable until 1872, when William Willis junior (1841–1923), of Bromley, Kent, (fig. 1.1) took up the challenge in search of a more enduring photographic permanence than silver images had afforded. Willis was born in 1841 at St. Austell in Cornwall, the elder son of William Willis Senior (1814–1883), an engraver of landscapes. In 1864, while the family was resident in Birmingham, Willis Senior invented the ‘aniline’ process for reprographic copying of architectural plans and engineering drawings.⁴⁷ This represented a union of Mungo Ponton’s invention of the light-sensitive dichromated paper process of 1839, with the discovery of the first aniline dye, mauveine, made by the dichromate oxidation of aniline, in 1856 by William Henry Perkin (1838–1907). The UK patent rights were purchased from Willis by the photolithography company of Vincent Brooks (1815–1885) in 1866.⁴⁸ The modest premises provided for their aniline printing works in 1867 are shown in a photograph, figure 1.2, from which the author has identified their location as the village of St Mary Cray, in Kent,⁴⁹ where Vincent Brooks also had his family home, as described in the autobiography of his son.⁵⁰



Fig. 1.2 “Place where Mr Willis made his aniline pictures – Received from him about 1867–8.” (Caption on the recto) Photographer W. Willis Snr? Courtesy of the J.W. Osborne Collection of the Smithsonian Institution, National Museum of American History, Washington DC.⁵¹

In the detail, fig. 1.3, the printing-out frames are seen to be much larger than any camera negative, indicating that drawings were being photocopied. It is highly probable that the 'apprentice' figure in the photograph taken *ca* 1867 is William Willis Senior's employee, Alfred Clements, then aged about 21.⁵² Compare his likeness with the portrait thirty or so years later in fig. 1.3a.



Fig. 1.3 Detail of Fig. 1.2 Apprentice with printing-out frames, 1867.



Fig. 1.3a. Alfred Clements, portrait taken ca. 1903

In 1867 the American patent rights for Willis's aniline process⁵³ were bought by Edward Anthony of E. & H.T. Anthony & Co., representing the American Photo-Lithographic Company of Brooklyn, New York; consequently in 1868 Alfred Clements was sent to the USA charged with the task of operating the process there.

The print from the archives of the Smithsonian Institution, shown in fig. 1.2, was probably conveyed to the USA by Clements himself; it is captioned on the verso: "Mr. Willis' Shop"⁵⁴ and signed by J.W. Osborne, who donated his print collection to the Smithsonian Institution in 1888.⁵⁵ Osborne had arrived in the United States in 1864 and had set up the American Photo-Lithographic Company, remaining as its superintendent for a decade, so he was Clements' employer for some four years, hence the likely provenance of this photograph. The aniline process enterprise turned out to be unsuccessful, however, so Clements turned his attention to photolithography, and after four years service, he changed his employer to the New York Graphic Company in 1872.⁵⁶ Alfred Clements is due to re-emerge as an important figure in our narrative in five years time (§1.10).

While in Birmingham, William Willis junior was trained and employed in engineering and banking,⁵⁷ before the family relocated to Kent around 1872, when he chose to take up his father's interests and engage with the problem of photographic impermanence. Willis then devoted himself to research in his private laboratory in Bromley, Kent, in order to perfect his Platinotype process, which would prove to absorb twenty more years of his life.

It follows that, counting from the dawn of photography, more than fifty years in all were to elapse before a viable commercial platinum printing process became well-established in 1892; but by 1916 the platinotype process had practically died out again. Our first historical task then is to resolve this paradox: **Why, in the entire history of photography, did its finest printing process come so late upon the scene, and then depart so early?**⁵⁸ The latter part of this question will be answered in Chapter 2, but the answer to the first part is as follows: Willis's ultimate success can be seen retrospectively to depend upon three key chemical innovations involving his correct choices of platinum salt, the light-sensitive iron salt, and the developer. No-one can hope to understand the historical development of the Platinotype process without some slight background in the chemistry of platinum, so this will now be explained using as little chemical jargon as possible, and avoiding arcane formulae, which the chemical enthusiast can discover in §11. The essential relevant facts may be exposed step by step in five simple chemical reactions.

First, metallic platinum has to be dissolved; the only common reagent capable of this is a formidable mixture of concentrated hydrochloric and nitric acids called, since alchemical times, *aqua regia*:⁵⁹



The resulting salt, previously referred to as 'platinic chloride' or 'platinum perchloride', was the only easily accessible compound of platinum known in the nineteenth century, and it provided the starting material for all early experiments in platinum chemistry.⁶⁰ It is fairly difficult to reduce this salt back

to the metal, however, and consequently it does not work as a satisfactory ingredient for a platinum printing process. Willis, in retrospect, described his first attempts in 1872 thus:

"All my early experiments were naturally made with platonic chloride."⁶¹

Like all previous experimenters, he began with the most readily available salt, platonic chloride, and achieved the disappointing kind of result we see in fig. 1.4. The subsequent deterioration of this specimen is a consequence of the facts that "platonic chloride" is strongly acidic and oxidising, and the paper was not washed.

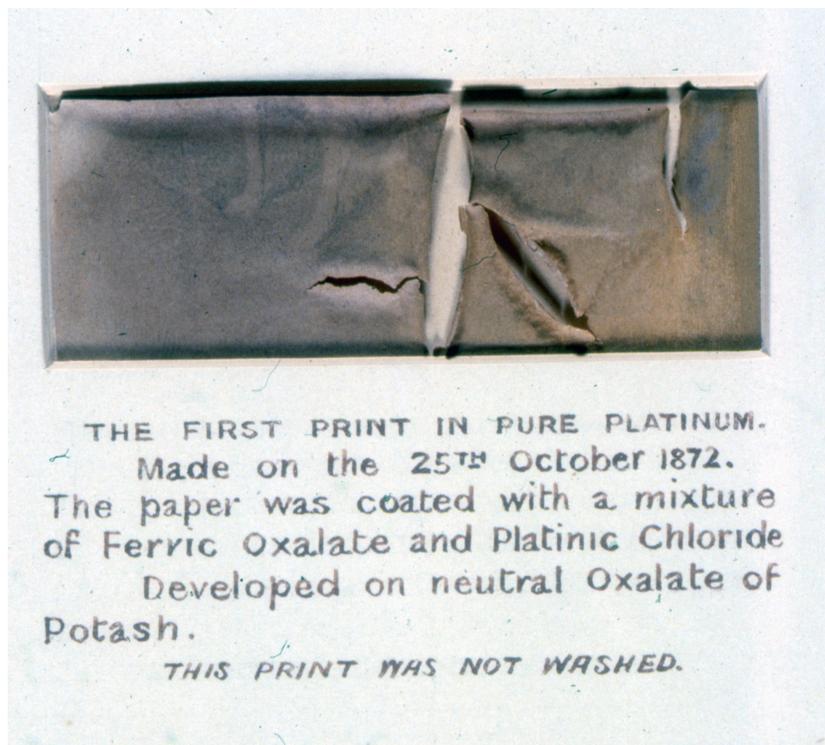


Fig. 1.4 "The first print in pure platinum"
 Collection of the National Media Museum, Bradford, UK.

Then, in 1873 Willis had the idea of turning from the usual platonic salts to the then little-known platinous salts which should be more easily reduced to platinum metal. Platinous chloride was obtained by partial reduction:⁶²

platonic chloride + reducing agents → platinous chloride

Although the preparation of platinous chloride⁶³ had been first reported by the German chemist Heinrich Gustav Magnus as early as 1828,⁶⁴ his method was difficult and uncertain, so this salt had remained a rare substance until the 1870's. As Willis in 1888 recalled retrospectively:

"After a troublesome operation, I made some potassic chloro-platinite."⁶⁵

It is this compound, platinous chloride, in its complex form as potassium chloroplatinite,⁶⁶ that is essential to a successful platinum printing process,

because it is more easily reduced than platinum chloride to the metal, producing it in the form of a nanoparticle 'platinum black' image, see fig. 1.5.

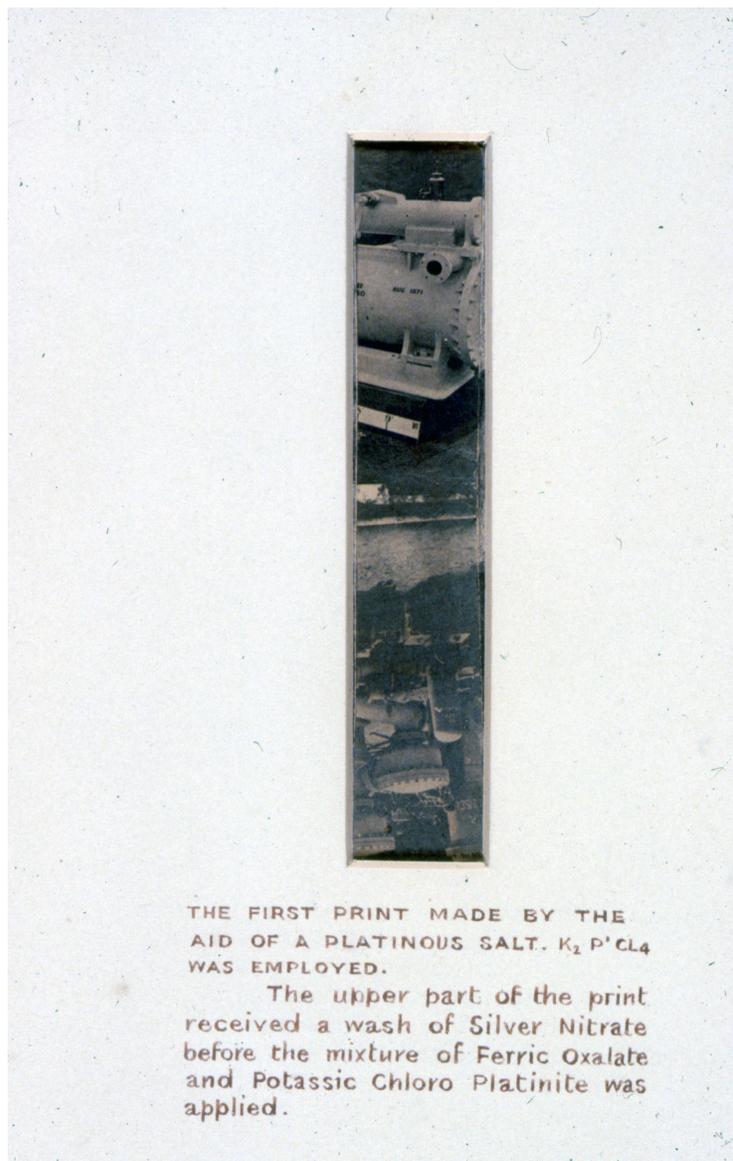


Fig. 1.5 "The first print made by the aid of a platinous salt."
Collection of the National Media Museum, Bradford, UK.

The importance of this breakthrough was later acknowledged by the chemist Chapman Jones in the context of the history of platinum toning of silver images:

"...it was not until potassium chloroplatinite was made available by Mr. Willis and the Platinotype Company that platinum toning was successful."⁶⁷

Indeed, Willis's finding a practical use for this expensive substance may account for the increased interest shown thereafter by preparative inorganic

chemists in devising easier syntheses of the little-known potassium chloroplatinite, using a variety of reducing agents.⁶⁸

Willis's second key choice was to employ the iron salt, ferric oxalate, which showed a sensitivity to light first discovered in 1831 by the German chemist Johann Wolfgang Döbereiner (1780–1849) as mentioned in §1.2,⁶⁹ whose picturesque description of this important experiment may be found in English translation.⁷⁰ The exposure of ferric oxalate solution to light results in the precipitation of the insoluble solid ferrous oxalate dihydrate, also known as the naturally-occurring mineral Humboldtine (or Humboldtite):

ferric oxalate solution + UV light → ferrous oxalate solid + carbon dioxide gas

We note that this uncommon salt did not feature in Herschel's siderotype experiments of 1842, which employed the much more readily available salt, ammonium ferric citrate.⁷¹ Although the latter suffices to produce gold, silver, and mercury images, as we have seen, ferrous citrate is not a sufficiently powerful reducing agent to enable a similar platinum printing process. Hence the successful platinotype sensitizer had to employ the more energetic ferric oxalate as its light-sensitive component. The use of this salt for photography also had a substantial previous history, because it was advocated first by Robert Hunt in his famous volume *Researches on Light* of 1844,⁷² although it was never taken up by Herschel for his siderotype processes (§1.3). It seems a likely speculation that William Willis would have been aware of this publication by his fellow-Cornishman, Hunt.

The third component essential for Willis's Platinotype process was a 'developer', potassium oxalate, to dissolve the insoluble ferrous oxalate produced by light, providing a strongly reducing solution:

ferrous oxalate + potassium oxalate → soluble ferrous oxalate complex
which could then reduce the platinum salt to platinum metal. Willis admitted that his attention was directed to try potassium oxalate for this purpose by:

"...a note by a French chemist..."⁷³

who regrettably has always remained unidentified. Willis also had to prepare the potassium oxalate for himself because at the time, surprisingly, he could not obtain this substance in London.

Once in solution the ferrous oxalate is a sufficiently powerful reducing agent to form the platinum image by the following reaction:

potassium chloroplatinite + ferrous oxalate complex → platinum black

Thus, we can identify in Willis's work three chemical causes for the historical time-lag in developing a viable Platinotype process: first, it was the unavailability at the outset of the key platinum chemical, potassium chloroplatinite; second, the need for the 'rare' substance ferric oxalate as the effective photosensitizer; and third, the use of potassium oxalate as a developer. These inhibitions, however, only marked the beginning of the difficulties that Willis had to overcome. The reaction by which the platinum image is formed proceeds relatively slowly; in consequence, during wet

processing some of the chemicals may be washed out of the paper before the reaction is complete, causing a loss in the quality of the image, which takes on a 'granular' or 'fibrous' appearance. In search of a means to accelerate the image-forming reaction and achieve a fully-developed picture quality, Willis was obliged to compromise the elegant simplicity of his original idea by adding to his sensitizer formulation salts of lead, silver (see caption to fig. 1.3), gold or mercury, which he found assisted the image formation (for the chemistry of this see §11.9).

A few specimens of these early experiments by Willis from 1873 came to light in 1988 at a Christie's sale.⁷⁴ They were subsequently kindly donated by Hans P. Kraus Jnr of New York to the Photograph Study Collection of the National Gallery of Art, Washington DC, where studies by XRF revealed the presence of gold and silver as well as platinum in the images.⁷⁵ See fig. 1.6. Such uncertain mixtures – especially with silver – won little public acceptance for his process initially, and the presence of these other metals left the Platinotype open to the criticism that it could be discoloured by sulphides, see §9.1. Nonetheless, Willis took out a patent on 5th June 1873 entitled *Improvements in Photo-chemical Printing* (for full text see Appendix VII), which was greeted with editorial acclaim in *The British Journal of Photography (BJP)* of January 1874 as a "new printing process".⁷⁶

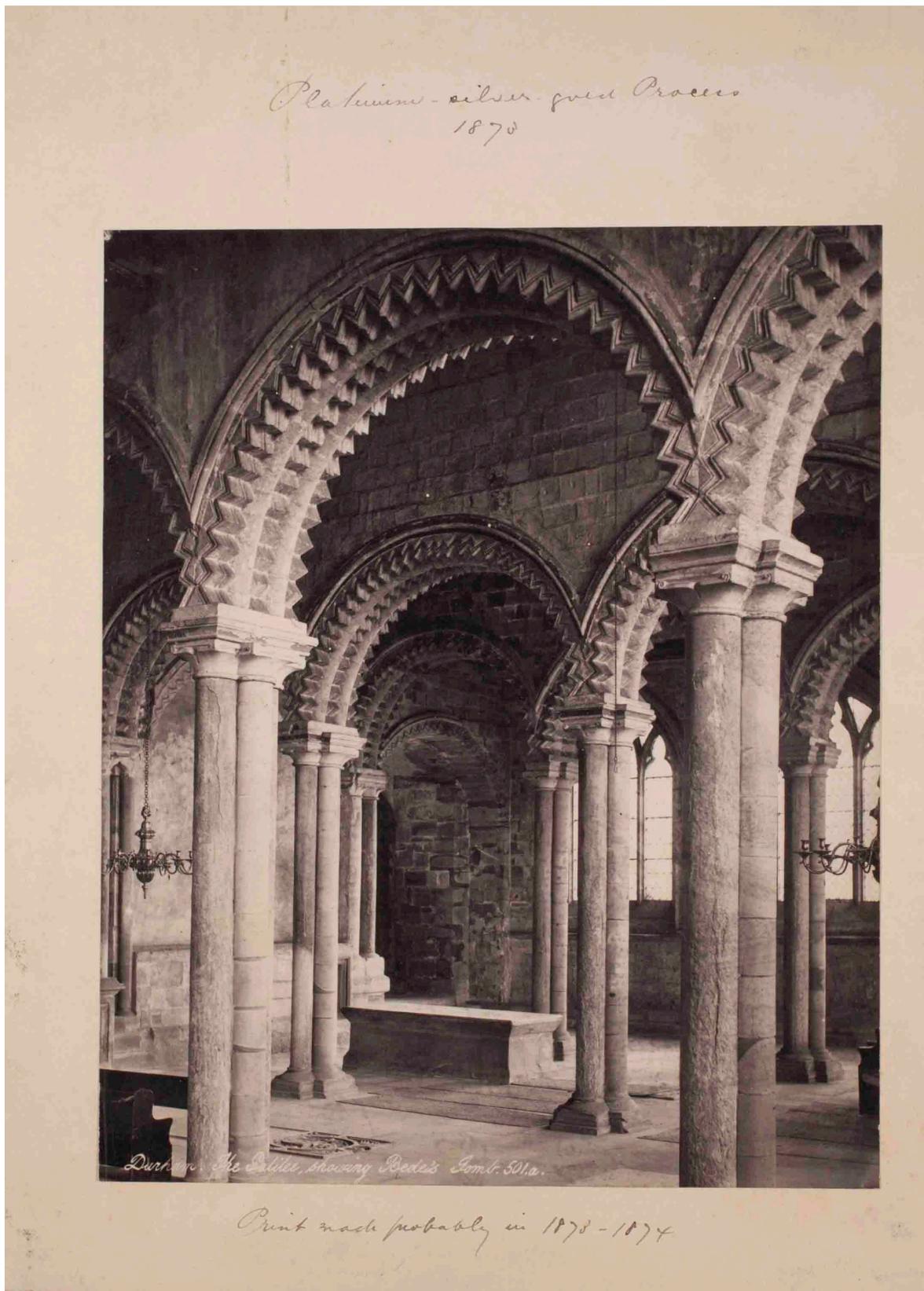


Fig. 1.6 William Willis "Platinum silver gold process" print 1873. Photograph Conservation Study Collection of the National Gallery of Art, Washington DC. Gift of Hans P. Kraus Jnr.

Almost nothing was then heard of Platinotype until 1877 when the process was demonstrated in public, probably for the first time, before the Edinburgh Photographic Society by Dr. Thomas Rodger, who also pre-coated the paper with silver nitrate, as reported in the *BJP*.⁷⁷ 1877 was also the year of Willis's first trip to the USA (§1.10), and during his visit to New York, Willis himself made the first Platinotype in the USA, which is shown in fig. 1.7.

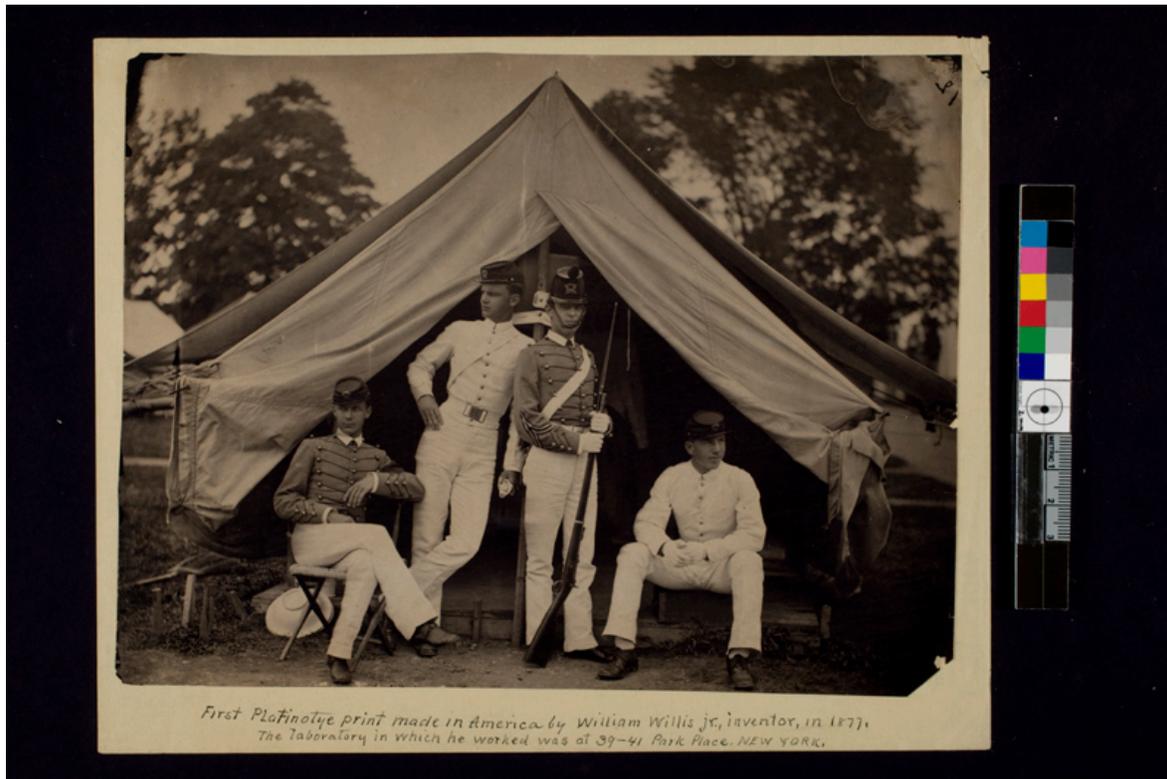


Fig. 1.7 "First Platinotype print made in America by William Willis jnr."
Collection of George Eastman Museum, Rochester NY.

The original, now in the collection of George Eastman Museum, was analysed by Dusan Stulik and Tram Vo in 2010, using X-ray fluorescence spectrometry, (see §5.5) and they reported as follows:

" The GCI team had a chance to analyze the GEH platinotype and determined that Willis had made this particular photograph still using his original platinotype formula patented in 1873. Willis' improved and "silverless" platinotype process was patented in 1878. It is theorized that he was already working with the new formula in 1877 but had not yet obtained good or consistent results, and so he opted to use his original and well-tested formula for his New York demonstration." ⁷⁸

We may infer from this comment that Stulik and Vo found silver in the print, as well as platinum, and it has been subsequently confirmed that "they detected trace amounts of silver in the analysis". They do not mention whether lead or mercury were also present. However, the speculation that Willis was already working with a silverless process in 1877 is disproved by the evidence in §1.7. A re-examination of the print in 2015 by conservator Zachary Long at

GEM has indeed proved that, to enhance the platinum image, not only did Willis add some silver, but also gold – just as Clarke has found in the earliest of Willis’s experimental prints, shown in fig 1.6. It appears that when making this historic “Platinotype” print in the USA, Willis was prudently “hedging his bets”!

Evidently, progress did not prove easy for Willis; his endeavours with Platinotype spanned twenty years of research in his private laboratory, and his struggles with the recalcitrant chemistry of platinum can be traced through five British patent specifications from 1873 to 1887 (see transcripts in Appendix VII),⁷⁹ which have been quoted *in extenso* by Luis Nadeau in his valuable monograph on platinum printing,⁸⁰ and transcribed by Ian Leake.⁸¹ We are also fortunate to have specimens illustrating the early development of the process (see figs. 1.2 and 1.3) in a panel prepared by Willis himself for the International Exhibition of Inventors in 1885 and subsequently lent by him to the Science Museum (it is now in the National Media Museum).⁸²

1.7 Willis's Platinotype Company of London

In March 1878 Willis succeeded in eliminating the silver from his sensitized papers, but at the cost of adding some potassium chloroplatinite to the developer bath in order to sustain the image quality. The first attested example of this advance is the remarkable double print shown in figure 1.8.⁸³ This silver-free platinum print is now in the collection of The Metropolitan Museum of Art, New York. For a description of its provenance, Christie's auction catalogue can be consulted.⁸⁴ The verso of this print bears annotations in Willis's hand, first in pencil:

"1° Starch & 12 gr O.P
2° 10 gr Acetate of Lead
3° Sensit^d with
1 part Pt
1 part neutral Fer Ox
~~1 part gold~~ [illeg.]
Not toned"

followed in ink by:

"First print made by the above process in platinum alone without aid by silver salts. Mch 17/78. W. Willis Jnr."

"Witnessed development of above W. Mansfield March 17/78" ⁸⁵

Later in 1878, Willis patented, then publicised this achievement of “altogether dispensing with the silver” in his process, which included some platinum salt in the developer, although he did also mention the addition of the salt, lead(II) chloride. Apart from his two patents of 1873 and 1878, his August 1878 article in *The British Journal of Photography (BJP)* appears to be his first publication on the Platinotype process, in which he provided an explanation of its underlying chemistry. Willis commended Platinotype for its permanence and the absence of any colloidal binder layer – qualities which, he said:

“...render the process peculiarly adapted for the permanent reproduction of important documents, archaeological records, medical, geological, botanical,

and other scientific phenomena; or for illustrating the results of military, naval, and engineering operations and for the illustrations of high-class books.”⁸⁶



Fig. 1.8 The first silver-free platinum print, March 1878
Collection of The Metropolitan Museum of Art, New York.

It may be a significant reflection on Willis's cultural viewpoint that he did not mention here the possibility of using Platinotype as a medium for photographic art, although in 1881 he would use the process to copy his own landscape pencil sketches (§1.13). Willis reinforced his first publication four months later by performing a “practical demonstration of the working of his new Platinotype process” before a meeting of the Photographic Society of Great

Britain on 10 December, which was reported in *The Photographic Journal* dated 13 December 1878,⁸⁷ and published in the December issue of the *BJP* with explicit formulae for his sensitizer and developer solutions, which will be considered in §5.1.⁸⁸

This advance proved to be a turning point for Willis. Having eliminated the only perceived weakness, the silver-free process now met with the approval of photographic chemists such as Jabez Hughes. So, in 1878 Willis was sufficiently emboldened to found the Platinotype Company in order to market his Platinotype papers commercially.¹ It should be noted that all the histories of photography (e.g. Gernsheim⁸⁹) cite 1879 as the year of the establishment of the Platinotype Company, but 1878 is clearly stated on their official headed notepaper,⁹⁰ and this year is confirmed by the legend embossed on the lids of some Platinotype paper tins: "Established 1878".⁹¹ The Company operated initially from premises at 2, St. Mildred's Terrace, Bromley Road, in Lee, near Bromley in Kent,⁹² but by 1883 it had established a sales office in central London,⁹³ and a factory at Penge in the suburbs.⁹⁴ The first commercial Platinotype papers became available in Britain in 1879, with a choice of rough or smooth surface, on medium or thick paper at a price of one shilling for a Demy sheet 17.75 x 22.75 inches;⁹⁵ other sizes could be supplied *pro rata* at a unit cost of ca. 4 'old' pence per square foot (d/ft²).⁹⁶ The product did not meet with universal approbation, however, and the Platinotype Company had occasionally to defend itself in the photographic press, for instance against the observations of Mr. Andrew Pringle (see §9.1), one of its most persistent critics.⁹⁷

Platinotypes were probably first seen publicly in London in 1879, at the 24th Annual Exhibition of the Photographic Society of Great Britain, where Willis exhibited twelve Platinotypes that he had personally printed from negatives by Frederick Hollyer, Payne Jennings, Professor E. Stebbing and Valentine Blanchard.⁹⁸ These prints were well thought of by the judges and, together with three platinotypes by Professor Huggins, received "honourable mention".⁹⁹ Similar – or possibly even the same – Platinotypes were also exhibited, and admired for their matte surface, at the Royal Cornwall Polytechnic Society, which awarded Willis its silver medal for his process in 1879.¹⁰⁰

In an address to the Edinburgh Photographic Society in 1880, Willis explained that he had further simplified his process by omitting the lead salt altogether, and increasing the concentration of the platinum salt.¹⁰¹ He had been obliged to do this following the results of experiments conducted by John Spiller in February 1880 on the permanence of Platinotypes, in which the only reagent found to cause any staining was ammonium sulphide, reacting with the small amount of lead salt present (see §9.1) to cause discoloration by lead sulphide.¹⁰² The photographic chemist, George Dawson, gave his technical

¹ *Etymological footnote 1: Although they have today acquired generic significance, the words "Platinotype" and "Palladiotype" (capitalised thus) were originally the registered trade names for the products of Willis's Platinotype Company. In this account they will be so distinguished from all other platinum and palladium printing papers (Pt/Pd papers, for short) either manufactured by other companies, or hand-made by the printer.*

appraisal of the newly improved process in 1880,¹⁰³ and Willis's latest modification also met with editorial approval in the *BJP* of July that year:

"...it is impossible to imagine anything finer than the warm, velvety blacks of some of the prints before us."¹⁰⁴

PHOTOGRAPHY MADE EASY
BY THE
PLATINOTYPE PROCESS
FOR
PERMANENT PRINTING

This process is equally adapted to either Amateur or Professional use, and enables the printing to be accomplished in **one-third** of the time usual with albumenized paper, while the subsequent operations may be completed in a tittle of time: indeed, a picture may be printed and finished within the space of **one hour**. The Papers are of various kinds, and may be either "rough" or "smooth," "black" or "sepia," tinted.

Platinotype produced more artistic pictures than any other method of Photographic Printing.

SEVEN PRIZE MEDALS

Have been awarded in recognition of the great value of the process, including the **Progress Medal** of the Photographic Society of Great Britain; also numerous medals for results at various Exhibitions at home and abroad.

HIGHEST AWARD
AT THE
International Inventions Exhibition,
THE GOLD MEDAL

"FOR EXCELLENCE OF RESULTS IN PHOTOGRAPHIC PRINTING."
"PRODUCED BY W. WILLIS' INVENTION."

The Platinotype Process is used by many of the most distinguished Artists and Photographers, both Professional and Amateur; by many Engineers, and at Works throughout the Country; also by various Government Departments.

The Prospectus, with List of Papers, &c., and other necessaries for the process—which are few, simple, and inexpensive (say 24s., including Paper)—may be had on application; also INSTRUCTIONS.

THE PLATINOTYPE COMPANY,
29, Southampton Row, High Holborn, W.C.

Sole Manufacturers of the well-known Sulpho-Pyrogallol, the best Developer for Dry Plates. Packed, 2/10.

Fig. 1.9 Early Platinotype Company advertisement of 1885¹⁰⁵

Earlier in 1880, James Young had demonstrated the Platinotype process to the Manchester Photographic Society and particularly commended it for its “engraving black” image colour.¹⁰⁶ A description of the operations of the new Platinotype Company was published in Henry Baden Pritchard's 1882 volume *The Photographic Studios of Europe*.¹⁰⁷

By 1885, the Platinotype process had been awarded medals for excellence, including a Gold Medal at the International Inventions Exhibition, see fig. 1.9.

Because the process was still protected by Willis's later patents of 1878 and 1880, all prospective users, both amateur and professional, were initially required to pay the Platinotype Company a five shilling fee for a licence to practise platinum printing, which is equivalent to about £20 today.¹⁰⁸ This tariff was suspended in 1888 after Willis launched his “new platinum-in-the-bath method”, protected by two more patents of 1887, see fig. 1.10.

THE COLD-BATH PROCESS.

THE SENSITISED PAPER for this NEW PROCESS for PLATINOTYPE PRINTING is Now Ready.

Under the Patents Nos. 1,681 and 16,003, A.D. 1887.

THE PLATINOTYPE COMPANY will permit those who use their SENSITISED PAPERS and PATENTED METHODS of DEVELOPMENT to do so without Licence or Fee, provided that the Sensitised Papers and Chemicals for Developing are in all cases obtained from themselves.

“THE PRINTING-OUT PROCESS.”

THE PLATINOTYPE COMPANY will also supply to their Licencees under Patent No. 1,117, A.D. 1880—and to those who in the future are Licenced to use this Patent—the Papers and Chemicals for preparing this Paper.

[The SENSITISED Papers for THIS Process will not be made by the Company: but they are willing to meet any demand there may be for the necessary materials.]

THE PLATINOTYPE COMPANY,
29, SOUTHAMPTON ROW, W.C.

Fig. 1.10 Advertisement for the “Platinum-in-the-bath” process, 1888.¹⁰⁹

In this innovation the paper was sensitized only by ferric oxalate together with a small, but apparently essential, quantity of mercuric chloride, and the development bath, which could be used cold, contained the usual potassium oxalate and all the potassium chloroplatinite.¹¹⁰ Unfortunately this was a recipe for failure. This latest version of the process proved commercially very short-lived – for barely four years – owing to an uneconomic defect, of which Willis was, in fact, aware at the outset:

“The constituents of this developer, when mixed in solution, undergo a slow mutual decomposition; hence it is necessary to mix them not too long before use.”¹¹¹

In responding to questions at the meeting of the London Camera Club where this process was announced, Willis admitted that both oxalate of platinum and platinum metal itself soon precipitated out from the stored developer, which quickly became black and unusable (the underlying chemistry is described in §9.13). Willis withdrew this “platinum-in-the-bath” method in

1892 when he launched his final, most successful version: "cold development" paper.¹¹²

1.8 Perfection of Platinotype

In 1892 Willis stated before the Camera Club of London that he had found a means to make fine Platinotype prints by development at room temperature, rather than at the elevated temperatures which had caused so many workers previously to scald their fingers:

"Now, I have recently discovered a method of preparing ordinary Platinotype paper, so that during development the rapidity of solution of the salts shall not overtake the rapidity of reduction – or, to express it differently – so that the image shall be developed before the salts which cause its formation have been removed from the paper.

For reasons which will be understood I cannot make this method public."¹¹³

It is eternally to be regretted that Willis chose to protect this version by secrecy rather than by taking out another patent. The preparative details for this unpatented paper were never disclosed, and no technical records of Willis's Platinotype Company (1878–1937) are known to have survived the London Blitz of World War II,¹¹⁴ so that today the manufacture of his most successful commercial papers is a lost secret. We may infer from Willis's words that the key to success lay in the sizing or coating of the "ordinary Platinotype paper", rather than in any innovation in the chemistry of the sensitizer. High quality papers made in Britain at the time were usually sized with animal gelatin, but Willis was aware from an early stage (ca. 1880) that this substance inhibited the chemistry of Platinotype. He therefore avoided gelatin as a sizing agent for his papers, and looked abroad to papers made in Germany and France, see §5.2, although his patents, being typically "economical with the truth", say nothing of this important choice. Accounts of the new paper published in the photographic press gave little away, beyond emphasising the convenience of cold development and praising the quality of its blacks and the robustness of the paper, its resistance to folding damage and immunity from forming "tide marks" when momentarily only partially covered with developer.¹¹⁵

But the success of 1892 must have entailed some additional feature, possibly the use of a retentive, acidic alum–rosin sizing for the paper, or the inclusion of a clay filler (§5.2), which slowed up the rate of dissolution of the exposed sensitizer during wet processing and allowed a full development of the image. Thus, after twenty years of intensive research, Willis had finally arrived at a Platinotype formulation that fulfilled his original conception of 1872, and he could sustain the proud claims of his advertisement (fig. 1.11) that his process was "Permanent, Artistic, and the Simplest". Passing over the guarantee of gaining medals – which might today appear contrary to the Trades Descriptions Act! – let us make a preliminary examination of his threefold claims.

1) The attribute of photographic permanence had been a longstanding issue ever since Henry Talbot recognised the vulnerability of his silver prints to fading and the aptly-named 'Fading Committee' of the Photographic Society¹¹⁶ recommended in 1855 that, for permanence, silver prints should be gold–

toned.¹¹⁷ A few years later in 1859 the Duc de Luynes funded a prize for devising a permanent photographic process, which was won by Alphonse Poitevin (1819–1882) with carbon printing. It was also the quest for permanence that stimulated Willis's platinum research in the first place, but even after he had finalised his procedures, we read many articles in the photographic literature complaining of stains due to incomplete clearing, and offering suggestions for curing yellowed highlights in Platinotypes.

vi THE PHOTOGRAPHIC NEWS ALMANAC ADVERTISEMENTS.

*If you wish to gain Medals,
If you wish for Permanent
Results,
If you wish for Artistic
Effects,
If you seek the
Simplest
Process,*

USE

PLATINOTYPE.

For full Particulars apply to
THE
PLATINOTYPE CO.,
29, Southampton Row, High Holborn,
LONDON, W.C.




Fig. 1.11 Platinotype Company Advertisement ca. 1898¹¹⁸

Although the metal constituting a Platinotype image is quite invulnerable, its paper substrate is certainly not: acidic embrittlement of the cellulose is the chief besetting problem that historic Platinotypes present to the conservator. The build-up of acid is exacerbated by the catalytic action of the platinum black itself, which assists the conversion of sulphur dioxide present in polluted

atmospheres into sulphur trioxide, and thence by an irreversible reaction with water to highly destructive sulphuric acid. These are issues which we shall take up in detail later in this work in §9.7.

During the 1880s Platinotype also came under criticism for being susceptible to sulphides causing yellowing of the highlights, which was probably due to the presence of other metals such as silver, mercury or lead, forming dark coloured sulphides as discussed in §9.1. Willis's patents reflect his attempts to overcome this problem, but the results of analysis show that lead was still present in some of his papers post-1892.

2) The "artistic" claim is also debatable: the Platinotype, with its neutral grey-black tones and totally matte surface, arrived at a time when the public taste in photographs had already been conditioned by an aesthetic of highly glossy purplish-brown gold-toned albumen prints, the dominant photographic print medium of the previous forty years. It is significant that the pigmented 'carbon' tissues of the Autotype Company also offered a popular colour to mimic this. The neutral tones of platinotype were often viewed with distaste, as typified by the comments of one, Leon Vidal:

"Platinotype prints are said with justice to be devoid of warmth, to have a cold, gray, and somewhat monotonous aspect whenever their slate-coloured tone is contrasted with prints upon albumen." ¹¹⁹

Although the general public tended at first to shun the Platinotype for its 'un-photographic' appearance, there were connoisseurs such as William Kinninmond Burton who appreciated its

"...fine engraving black without meretricious gloss." ¹²⁰

John Nicol published an eloquent polemic in 1879 against the superficial popular taste for "warm shades of purple-brown" in photographs, and favoured the neutral colour of Platinotype and commended its permanence.¹²¹ Herbert Bowyer Berkeley (1851-1890), who remained in partnership with Willis in the Platinotype Company until 1889,¹²² was more proactive in public relations than the retiring Willis, and expressed his views quite vigorously:

"The platinotype proces is nothing if not artistic. It claims the notice and enlists the sympathies of those who aspire to the 'beautiful' rather than to the 'pretty' ...silver prints, which, being 'sharp and slimy' cannot give the effect of atmosphere and distance as the plain paper does... He who glazes a platinotype commits an aesthetic sin..." ¹²³

In his slim monograph on *Platinotype Printing* (1897), Alfred Horsley Hinton also referred disparagingly to the glossy surface of albumen papers:

"The slimy appearance of albumenised paper, giving the print the appearance of a magnified snails' playground..."

and he revealed an attitude redolent with the class snobbery of the age:

"...if I have prints on platinotype paper and on a fine glossy-surfaced gelatine or albumen paper, and lay them before a child of twelve years, I expect him to show preference for the latter ... or if I show them to my servant or a person of less cultivation, again I shall be surprised if he does

not show preference for the print of high surface ... the silver print [is] extolled for the very qualities which the more advanced and more intelligent photographer has now long since come to regard as qualities better dispensed with ..." ¹²⁴

Nevertheless, the loss of brilliance and shadow depth on drying a plain-paper platinum print induced some practitioners to resort to coating their prints after processing. Conservator Clara von Waldthausen has described the various materials recommended in this practice,¹²⁵ which could include jelly size, varnish, beeswax or water megilp.¹²⁶

Willis's commercial awareness of popular public demand induced him to respond by devising and marketing Platinotype papers to furnish prints that were brown - "Sepia Platinotype", see §1.9, or semi-glossy - "Japine paper", see §1.15, or even both - "Sepia Japine".

3) Regarding the claim of simplicity for Platinotype, it had to be admitted that the *modus operandi* was certainly much easier than silver printing-out paper, which required three times the exposure, very careful wet processing, and gold toning for permanence; by contrast, a finished platinum print could be obtained in half an hour, or even much less if performed "sloppily", as we shall see in §3.2. We find evidence in published manuals of photography that the process was highly popular and strongly recommended for beginners - a view that is typified, for instance, by this quotation from *Photography for Novices*:

"...platinotype is the simplest and quickest process of printing..." ¹²⁷

The cost was also fairly competitive, at least initially: in 1892 a 10"x12" sheet of Platinotype paper cost 6 pence,¹²⁸ compared with 5 pence for a corresponding sheet of silver bromide enlarging paper.¹²⁹

William Willis, having invested much effort over many years in perfecting the process, was always cautious in guarding the detailed manufacture of his platinotype paper, and he published no formulae other than those summarised in his patents. He rarely allowed visitors on his factory premises, with the notable exception of a group of about 150 members of the Professional Photographers Association, who on 19 May 1911 were shown over the factory in Penge for the first time in the Company's history - an event that was widely reported in the photographic press, whose descriptions convey some impression of the professionalism of Willis's production methods and the scrupulous cleanliness of the coating works.¹³⁰ This 'Open Day' was repeated successfully in November 1911, for another, less formal group of visitors from the local Croydon Camera Club.¹³¹ However, the most detailed description of Willis's factory and works at Penge comes in 1915 from the anonymous 'Roving Commissioner' of the trade journal, *The Photographic Dealer*.¹³²

One of the priorities of recent contemporary research has been to infer likely compositions for Willis's final (1892) versions of his Platinotype papers, by searching the historical literature, by chemical and spectroscopic analysis of historic specimens, as reported in §5 for both reference prints and unexposed papers of the time, and by attempted simulation of the processes, as will be described in §6.

1.9 *Sepia Platinotype with mercuric salts*

It is sometimes mistakenly stated that "sepia platinotypes" were simply made historically by employing a hot developer bath, at ca. 160°F (71°C).¹³³ However the degree of "warming" of the neutral grey–black colour of normal "cold bath" Platinotype paper achieved by this means is found to be only "very slight". It is clear from Willis's published comments to the Camera Club that he had, from an early stage, been seeking a formula for sepia Platinotype paper as a commercial alternative for those who disliked the black variety. It was stated in his patent description of 1878 that a small quantity of mercuric chloride could be added to the developer solution, which had to be used hot at 140–160°F, but the chief disadvantage of this turned out to be a resulting shift of colour between the brown high values and the neutral dark shadows, which Willis called "double tones", and which he found aesthetically unacceptable. This problem may account for the fact that sepia Platinotype paper is not mentioned in the earliest advertisements and instructions from the Platinotype Company, but was probably first marketed *circa* 1885, to judge by the advertisement of that year (Fig. 1.9). Willis had discovered a formulation for including the mercuric chloride in the sensitized coating, that did not suffer from the disadvantage of "double tones". Hot development was necessary, as with the black papers at that time, and although not essential, it was also recommended that for the best results a small amount of the Company's "Special Sepia Solution" (a trade secret) should be added to the usual oxalate developer bath, to achieve "a rich, bright sepia colour". Alternatively, the developer could be made up using the Company's proprietary "Sepia Crystals". It is likely that both of these preparations contained mercury salts. Although most of Willis's patents are rather ambiguous concerning his sensitizer formulations, his patent of February 1887 (Appendix VIII) states:

" I find the mercuric salt [mercuric chloride] very useful where a warm tone or effect somewhat resembling sepia is desired."

and he admitted to the Camera Club, in answer to questions, that the sepia colour was best brought about by including mercuric chloride in the sensitizer coating, rather than the developer, to avoid "double tones":

"You will remember that the earliest of the platinum sepia processes I introduced was one in which the paper used was simply the same as that which would develop black, but some mercuric chloride was placed in the developer...

... where the ferrous image is strong a black colour will be developed for there will not be enough mercuric chloride in contact with it to have the same effect relatively as on the other parts. ***In using a paper in which the sepia-giving agent - mercuric chloride - is present throughout the sensitive coating in its proper proportion***, a different action would take place." ¹³⁴ [my emphasis]

In 1892 it transpired that Willis's new cold development process for black paper was not applicable to his sepia papers, despite his endeavours in that direction; his publication admits that:

"...he was, however, doubtful whether sepia would ever be obtained under a temperature of 150°F." ¹³⁵

In 1893 Willis further confessed:

"To make good sepia paper is a heart-breaking problem, so much so indeed that I have rarely had the courage to attack it." ¹³⁶

but he then went on to describe his experiments with developers in the hope of finding a cold developed sepia paper, discovering that the inclusion of glycerine in the developer enabled its use at lower temperatures.¹³⁷ Nonetheless the Platinotype Company product lists (in 1894 and in 1906) continued to designate it as "sepia hot bath paper", grades S and RS (see §1.14), and by 1911 these commercial sepia papers still had to be developed at 160–170°F (71–77°C), for preference.

In his important review of 1911,¹³⁸ the Platinotype Company manager W.H. Smith warned that if an excessive amount of mercuric chloride was added to the developer bath in the hope of generating sepia tones from "black" papers, the colour would turn out to be disagreeable and the image would prove impermanent. Smith averred that:

"The Platinotype Company had never advocated the use of mercury in their developers simply because it was not stable, and they would not include a formula in their instructions which would injure the reputation of platinum printing for permanency." ¹³⁹

In a commentary on Smith's lecture the same year, F.C. Lambert remarked that a novel point to him was that mercury-developed sepia images were soluble in a solution of sodium thiosulphate and potassium ferricyanide (Farmer's reducer, used in silver photography).¹⁴⁰ At a later meeting in 1915, Smith showed severely faded specimens of mercury-developed Platinotypes to demonstrate his point.¹⁴¹ In spite of this warning, he described the addition of modest amounts of mercuric chloride to the developer in order to warm the otherwise neutral image colour of "black" platinotype, and many practitioners of the day did indeed resort to this practice, as it was recommended by Paul Anderson in 1917:

"Warmer Tones. — a slight increase in warmth of tone is secured by using a hot developer, and commercial papers may be obtained in which the sensitizing has been such as to give sepia prints. The writer, however, prefers to use the black papers and secure warmer tones by modifying the developer ... The addition of a slight amount of bichloride of mercury to the developer produces a warm black, and further additions may increase the warmth of color up to a full sepia ... Some writers say that the addition of bichloride of mercury causes instability of the results, but the writer has not found this to be the case in his own practice, which extends over a period of about ten years ... it has been stated on the authority of von Hübl that the image in a mercury developed platinum print consists of pure metallic platinum, the warmth of color being due to a difference in the size of the grains of metal deposited ... if it is correct there is, of course, no reason to fear fugitiveness of a brown or sepia platinum ... this instability is due to insufficient clearing, so that some iron salts are left remaining on the paper,

these salts of course darkening when exposed to light. This belief is supported by the fact that most writers recommend clearing such prints for not more than two minutes in a single bath of Water 300 ounces, Hydrochloric acid C. P. 1 ounce, since it is undeniably the case that a normal clearing bath will remove some of the warmth resulting from the use of mercury." ¹⁴²

This passage from Anderson's influential book does tend to perpetuate the misconception that there is no mercury in sepia platinotypes, which we now know to be wrong from X-ray analysis (§5.9). However, there is no doubt that he was right in pointing out that such a dilute acid clearing bath would leave much residual iron in the paper. He did not, however, ask why a normal strength of acid clearing bath should so damage the image, if it was indeed constituted of pure platinum.

Meanwhile, Baron Arthur von Hübl in the second edition (1902) of his work, *Der Platindruck*, (§1.16) had described an apparently novel formulation that finally enabled the cold development of sepia papers by using mercuric citrate rather than mercuric chloride in the sensitizer, and this recommendation eventually reached the popular handbooks.¹⁴³ Practical details of sepia platinotype are given in §6.7, and a consideration of the chemistry in §11.9.

1.10 Willis & Clements Company in the USA

On his early visit to the USA in 1877, mentioned in §1.6 above, William Willis Junior renewed his acquaintanceship with the expatriate Briton, Alfred Clements,¹⁴⁴ who had been sent to the USA ten years previously to work the reprographic 'aniline' process by William Willis Senior, as recounted in §1.6. During his time in the USA, Clements had kept in touch with the Willises, father and son, and on the occasion of his visit, William Junior seized the opportunity to form a partnership with Clements, who undertook to introduce the new Platinotype process to photographers in the USA.¹⁴⁵

Setting up business in New York,¹⁴⁶ Clements confined himself initially to retailing the chemicals for users to self-coat their own papers, and he was active in instructing them in the best techniques, so that by 1879 one satisfied user was reporting:

"It was my privilege to both see the process worked and to work it myself, and I can conscientiously say that a more simple process I have never tried."
¹⁴⁷

In 1879 Willis's Platinotype Process was also tentatively reviewed in the American photographic press, where its simplicity and permanence were approved, but some doubts were expressed over its aesthetic qualities:

"...the results, though soft and rich, are black and cold, and moreover their surface is mat, though some we have seen have been albumenized after printing, but with indifferent effect."¹⁴⁸

By 1880, Willis & Clements were advertising their services to print enlarged Platinotypes (see §1.11 and fig. 1.12), proudly boasting that:

"Ours is the only Electric Light used in the United States for this purpose."¹⁴⁹

them. Size of machine, about ten inches square; weight, less than 30 lbs. Handy for the counter; small children can incase their own pictures; requires no practice. Upwards of 250,000 of the portraits have been taken at the extensive galleries of Mr. Applegate, in Philadelphia. Price, with room light, \$40, C.O.D., or on receipt of P.O. order, including 200 specimens, enabling parties to commence operations immediately. Also, suitable Gem Cameras, furnished with six tubes, very low. Silver-plated rims, \$5 per 1000. Stock dealers supplied. Sample pictures sent by mail.

Caution to Infringers.—This is the original machine, invented for this purpose by J. R. APPEGATE. It has been improved and patented, and all infringements on the same will be rigidly prosecuted.

FOR SALE BY **WILSON, HOOD & CO., Philadelphia Trade Agents.**

PLATINUM ENLARGEMENTS

BY THE ELECTRIC LIGHT.

By the use of the Electric Light we have succeeded in making ourselves independent of sunshine, and are, therefore, enabled to execute promptly all orders which may be sent to us. Our Platinotype Enlargements are well known for their

Purity, Vigor, Half-tone, Color, and Absolute Permanence.

PRICE LISTS AND PARTICULARS MAY BE OBTAINED FROM

WILLIS & CLEMENTS, 17 East 17th St., New York.

N. B.—Ours is the only Electric Light used in the United States for this purpose.

THE

Willis Platinotype Process,

WILLIS & CLEMENTS, 17 East 17th St., New York,
PROPRIETORS FOR THE UNITED STATES.

This is the *simplest* photographic process now in use. It is remarkable for its *rapidity* and the *certainty* of its results.

PLATINOTYPES ARE CHARACTERIZED BY A

Beautiful Tone, Perfection of Detail, Pure Whites, and Absolute Permanence.

Licenses to use the process issued, and all necessary materials supplied by the proprietors, from whom terms and detailed information may be obtained.

1

Fig. 1.12 Early advertisement for Willis & Clements 1880.

The technology of enlarging is further considered in the next section §1.11. Clements encountered many difficulties with it, however, not least the explosion of a boiler on 17th December 1880, which destroyed all of the equipment in the New York office on 26th Street.¹⁵⁰ In 1881 Clements gave up his enterprise in New York, offering the platinotype enlarging business for sale:

"THE PLATINOTYPE PROCESS— Messrs. Willis & Clements, finding it necessary to devote the whole of their time to the increased business of their manufacturing department, and to a great improvement in the process, shortly, to be introduced, have decided to dispose of their printing department. They are prepared to sell their solar and electric light department, including a license, apparatus, and good will. Purchaser can occupy part of their premises, and can have the benefit of their advice at all times. A large number of their orders for solar prints come from licensees, and these steadily increase in number. All such orders will be transferred to purchaser. The improvement in the process above alluded to is in reference to contact-printing in metallic platinum on a collodion surface. Terms, etc., at 123 West 26th St., N. Y."¹⁵¹

Having sold up his Platinotype enlarging business in New York, Clements relocated to Philadelphia. There he devoted his side of the business to manufacturing and retailing the chemicals for the Platinotype process and, since

it was by then protected by US patents, to the licensing of photographers in the USA to sensitise paper for their own use. An 1881 advertisement reads:

"THE PLATINOTYPE PROCESS— Having disposed of their printing business in New York, Willis & Clements will now devote the whole of their time to manufacturing chemicals for the process, and to instructing licensees in working. They have appointed Thos. H. McCollin, 631 Arch St., Philadelphia, sole trade agent for the sale of all special materials and apparatus used in the process. Willis & Clements will answer all letters of inquiry concerning the process. Agent. Thos. H. McCollin, 631 Arch St., Philadelphia, Pa. Proprietors of patents, Willis & Clements, 631 Arch St., Philadelphia, Pa. Note—On receipt of \$1.75, a small supply of chemicals and paper will be sent to any one desiring to try the process." ¹⁵²

Enlisting Thomas McCollin as a business agent in Philadelphia was probably a shrewd move, in view of his established reputation as a dealer in photographic materials and specialities, with a well-known catalogue, and by 1890 he was also the Managing Editor of the *American Journal of Photography*.

William Willis, too, made another trans-Atlantic trip in order to be personally involved in establishing Willis & Clements in Philadelphia: he is on record as addressing the Photographic Society of Philadelphia on 3rd February 1881, and conducting a public demonstration of the chemistry underlying his platinotype process.¹⁵³

The Philadelphia company retained the name of Willis & Clements, but did not begin to import Willis's pre-coated papers from Britain for some years. An early instruction booklet published in the USA by Willis & Clements, dating from 1885, shows that the Company was still confining itself to the retail of the sensitizer chemicals and paper needed to self-coat platinum paper by hand, together with other minor items of equipment.¹⁵⁴

Willis & Clements' instructions describe dissolving the solid platinum salt in their pre-prepared iron solutions (of unspecified concentration) immediately before coating with a squeegee. The Company prescribed different formulations for "contact printing" as opposed to "solar printing", using a solar enlarger, see §1.11. The Company's literature also encouraged the making of platinotypes on linen and cotton fabrics, such as nainsook (a very fine muslin), and even heavier fabrics such as jaconette and jean, sateen and oatmeal-cloth, (no doubt heavy absorbers of the expensive sensitizer solution) with the intention of decorating:

"d'oyleys, mats, banner-screens, antimacassars, cosies, mantel-cloths, &c" ¹⁵⁵

Silks and satins were not recommended unless they contained very little "dressing"; it seems that silk proved a more difficult substrate for Platinotype.

Alfred Clements made a visit to Europe in 1886,¹⁵⁶ after which the Willis & Clements Company finally began to import some of the sensitized papers of the Platinotype Company of London, and market them in the USA in 1888.¹⁵⁷ The paper was also offered by Buchanan, Bromley & Co., the importers (fig. 1.13).

The delay in beginning shipment of the paper to the USA may have been due to the poor keeping qualities of the coated paper, which needed to be rectified by Willis changing the packaging.¹⁵⁸ It is significant that the Platinotype paper at this stage (1888) was being distributed packaged in "light-tight

envelopes" (fig. 1.13) not the sealed tins containing desiccant that Willis soon found to be necessary to extend the shelf-life of his product, see §1.14, fig. 1.19.

Although "Sepia" Platinotype was featured in Willis & Clements first advertisements of their papers in 1888 (fig. 1.13), their subsequent price lists make no mention of the Platinotype Company's designated Sepia papers, alphabetically coded as Grades S and RS, and later as KS, TS, YS and ZS, (see §1.14, Table 1.1), which all contained mercury(II) salts – usually mercuric chloride – in the sensitized coating. Willis claimed that these sepia papers – although admittedly more susceptible and sensitive to light – did keep well, and possibly even better than the corresponding "black" varieties (see §1.14) of Grades KK, TT, CC, YY, and ZZ. It is hard to understand why sepia papers were not given their correct designations by Clements in the USA, but rather referred to as "Sepia KK" – presumably for Grade KS, etc.

The Platinotype Process.

*NO LICENSE IS NOW REQUIRED to use the Sensitized **Platinotype** Paper manufactured by Willis & Clements, Patentees.*

Prices for either "Sepia" or "Black" Sensitized Papers, Post-paid, in light-tight envelopes, well packed for mailing.

3 ¹ / ₄ x 4 ¹ / ₄ , per dozen.....	\$ 25	5 x 8, per dozen.....	\$ 75
4 x 5, "	50	6 ¹ / ₂ x 8 ¹ / ₂ , "	1 00
4 ¹ / ₄ x 5 ¹ / ₂ , "	50	8 x 10, "	1 50
4 ¹ / ₄ x 6 ¹ / ₂ , "	55	18 x 22, "	6 00
5 x 7, "	65		Discount, 20 per cent.

For Sale by all Dealers.

Buchanan, Bromley & Co. General Import and Export Agents,
PHILADELPHIA.

THE PLATINOTYPE.

(Patented.)

PLATINOTYPE "BLACK."
PLATINOTYPE "SEPIA."

For Professional Photographers and Amateurs.

A NEW DEPARTURE!

Send 10 cents in stamps for sample "Sepia"
or "Black" print and latest circular.

WILLIS & CLEMENTS,
913 Arch Street, Philadelphia, Pa.

Fig. 1.13 First Advertisements in the USA for Platinotype Papers, 1888 ¹⁵⁹

The Company's early difficulties with "sepia papers" were admitted by Alfred Clements in a lecture to the Photographic Society of Philadelphia on 8 March 1893:

"Regarding the Sepia process, I may say, that until recently we have been unable to satisfactorily supply the demand for this paper, on account of the many difficulties of manufacturing it. These difficulties are fast being overcome, and I can safely say, that we can now supply the paper and recommend its use."¹⁶⁰

In his *Camera Craft* article of 1906 on "Sepia Platinotype", Clements reiterates the condemnation of adding mercury(II) salts to the oxalate developer in order to produce sepia tones from "black" papers.¹⁶¹ It is therefore curious that his price list of 1908, fig. 1.14,¹⁶² still does not list the genuine Platinotype Company Sepia Platinotype papers, as Grades KS, TS, RS, YS and ZS, but continues to offer for sale so-called "Sepia" varieties of the Company's "black" papers of Grades KK, TT, CC, YY, and ZZ.

BLACK	BLACK	SEPIA	SEPIA
Med. Heavy, Smooth (BB)	Extra Heavy Smooth (YY)	Heavy Smooth (KK)	Extra Heavy Smooth (YY)
Heavy Smooth (KK)	Extra Heavy Rough (ZZ)	Heavy, Med. Rough (TT)	Extra Heavy Rough (ZZ)
Heavy, Med. Rough (TT)		Heavy Rough (CC)	
Heavy Rough (CC)			

Fig. 1.14 Platinotype papers from Willis & Clements Price List 1908.¹⁵⁸

The accompanying instructions make the clear proviso that their processing must employ the Company's proprietary "Sepia crystals" made up as a developer, or must entail the addition of their "Special Sepia Solution" to the developer, or preferably should use both measures.¹⁶³ These developer additives – of secret composition – presumably contained sufficient mercury(II) salt to render sepia tones on developing "black" papers.

Is it possible that the Company practiced a modest deception on its customers in order to provide them with a "Sepia" product line? Otherwise they would be seen to contradict their own strictures *against* using mercury salts in the developer, as previously described. From an existing specimen, it is apparent that Clements did re-label at least some of the Platinotype Company's tins of paper with Willis & Clements own labels. Another conjecture is that the tins of Sepia Platinotype paper did not last well enough for transatlantic shipping: it is possible that the presence of the mercuric chloride in the sensitized paper caused early corrosion of the tin containers; the substance was, after all, famously known as "corrosive sublimate". The issue awaits further evidence.

In 1906, it appears that the Company's "Japine Sepia Platinotype" paper (\$1.15) was made available in the USA, and received an enthusiastic endorsement from Charles Ogilvie in *Camera Craft*, as fulfilling a longfelt want.¹⁶⁴ "Sepia crystals" or preferably special "Japine" developer were again recommended, and the paper was said to have superior keeping qualities, a ten

times greater resistance to deterioration by moisture, and double the printing latitude of ordinary platinotype papers.

It is rather surprising that no mention is made of the Willis & Clements Company in the compendious promotional volume of 1889, *Illustrated Philadelphia: its Wealth and Industries*, although several other suppliers of platinotypes and of photographic equipment, such as Buchanan, Bromley & Co., do have entries.¹⁶⁵ This volume also describes the availability of platinotype enlargement services from a Mr. H. C. Bridle, of 913 Arch Street – an address used by Alfred Clements at the time – and two other photographers offering the service. The fact that Willis & Clements, over the years 1881–1928, conducted their business from at least ten different addresses in Philadelphia, also implies a curious – if not actually disquieting – mobility in the Company's premises.¹⁶⁶

1.11 Platinotypes by enlargement

As we have seen in fig. 1.12 above, the first pioneering experiments in enlarging onto Platinotype paper were made in early 1879 by Willis's transatlantic partner, Alfred Clements, in New York; this achievement was described by Willis to the Edinburgh Photographic Society and published in 1880.¹⁶⁷ Clements used at first a solar enlarger, and later the new electric light, an innovation employing a carbon arc and condenser lenses, which he learned about at the Technological Institute of Hoboken. According to Willis, using a 4.25 horsepower source, which is electrically equivalent to 3.17 kW, Clements exposures were 5 to 30 minutes, but the magnification was unspecified. The making of enlargements in Platinotype did not become a technique widely taken up by amateurs since it involved special optical equipment, but was confined mainly to professional printers in the USA, partly because of the better availability of the new electricity supplies, partly because of more sunlight for the solar enlarger, although the Platinotype Company in London also advertised the granting of licences for enlarging in 1884,¹⁶⁸ and Willis installed an enlarging facility in his Penge works which was described in 1911, and which required an exposure of three hours with a lens of f/3.5.¹⁶⁹

The solar enlarger – also called the solar camera – had been in use since it was introduced and patented in 1857 by American, David Acheson Woodward, as an adaptation of the solar microscope, which had been employed since the 18th century.¹⁷⁰ It collected the sun's light with a large plano-convex condensing lens enabled by an adjustable mirror to reflect the sun's rays into the optics; this required realignment every two minutes or so throughout exposures of some hours, to track the sun's apparent motion; more sophisticated models embodied a clockwork tracking mechanism called a heliostat. The focussed sunlight illuminated a negative mounted inside the camera body and its enlarged image was projected by an objective lens, preferably anastigmatic and of wide aperture, onto the sensitized paper surface. Despite the high intensity of the illumination, exposures by enlargement were necessarily much lengthier than those for contact printing, often running into hours, due to four contributing optical factors:

- the restricted aperture of the objective lens, the exposure time being proportional to $(f/\text{stop})^2$. A lens of f/3.5 was commonly described.

- the attenuation of image intensity due to the magnification, m , for which the exposure duration is proportional to m^2 .
- the absorption of UV by the glass lenses, which could present an optical path several centimeters in length; quartz lenses were preferred, but scarce and expensive.
- the strong Callier effect that comes into play when using a 'point source' of light with a condenser enlarger: the light rays are scattered off the optical axis by the silver particles in the negative so the contrast of the projected image becomes higher than it is by contact.¹⁷¹ A "thinner" negative could therefore still provide a sufficient effective density range to match the long exposure scale of the platinum sensitizer.

In an effort to maximise the sensitivity and shorten the long exposures needed, Willis & Clements offered "solar" iron solution – of concentration and composition unspecified, but they also recommended using a lower ratio of platinum salt to ferric oxalate, thus diminishing the 'internal filter effect' where UV is unproductively absorbed by the non-photosensitive component of the sensitizer, the platinum salt. The internal filter effect could be eliminated altogether by employing Willis's "cold bath" process which placed all the platinum salt in the developer bath, and therefore provided the most sensitive process.¹⁷²

In their Platinotype treatise, Abney and Clarke have a chapter on enlargement printing, with details of the optical paths, and they there claim short exposure times of 15 to 25 minutes with a carbon arc light source of 1100 candles (13,823 lumens), but this is achieved for a linear magnification of only 2x. The Callier effect is unwittingly acknowledged by Abney's observation: "a rather feeble negative ... will give the best results".¹⁷³ However, John A. Tennant, editor of *The Photo-Miniature*, tested platinotype enlarging with very similar apparatus and found that "The time required to get a barely perceptible image was just one hour."¹⁷⁴ In modern times, the printing of enlarged platinotypes has been achieved by Greta Glaser,¹⁷⁵ who points out that the procedure was probably only economic when single prints were required from negatives, and that for multiple prints the preferred strategy would have been the creation of an enlarged duplicate internegative for conventional contact printing. Glaser also replicated the projection enlarging process experimentally onto platinotype paper, using both solar and electric light sources; the historic solar instrument proved difficult to maintain over long exposures and only a faint image was obtained in two hours. Using a modern commercial condenser enlarger with UV LED light source and quartz optics, a six hour exposure was needed to produce a satisfactory enlargement from a 35 mm negative with a linear magnification of 2.7x.

1.12 Notable early users

It was not until Willis's advance of 1892 that the Platinotype process was generally acclaimed by the photographic press in Britain, thus ensuring that Willis's product enjoyed a much wider use. By 1895, more Platinotypes than any other photographic process could be seen on the salon walls in Britain: the

medium had finally achieved pre-eminence for art photography. As quantitative evidence for this claim, we have some exhibition statistics. Figure 1.15 displays the relative numbers of prints in three media, platinum, carbon and silver, shown at the prestigious Annual Exhibitions of the Royal Photographic Society between 1893 and 1901. The bar-chart demonstrates that between a half and a third of the work exhibited during those years was in platinum, the nearest competing process being carbon, with a quarter to a third of the total.

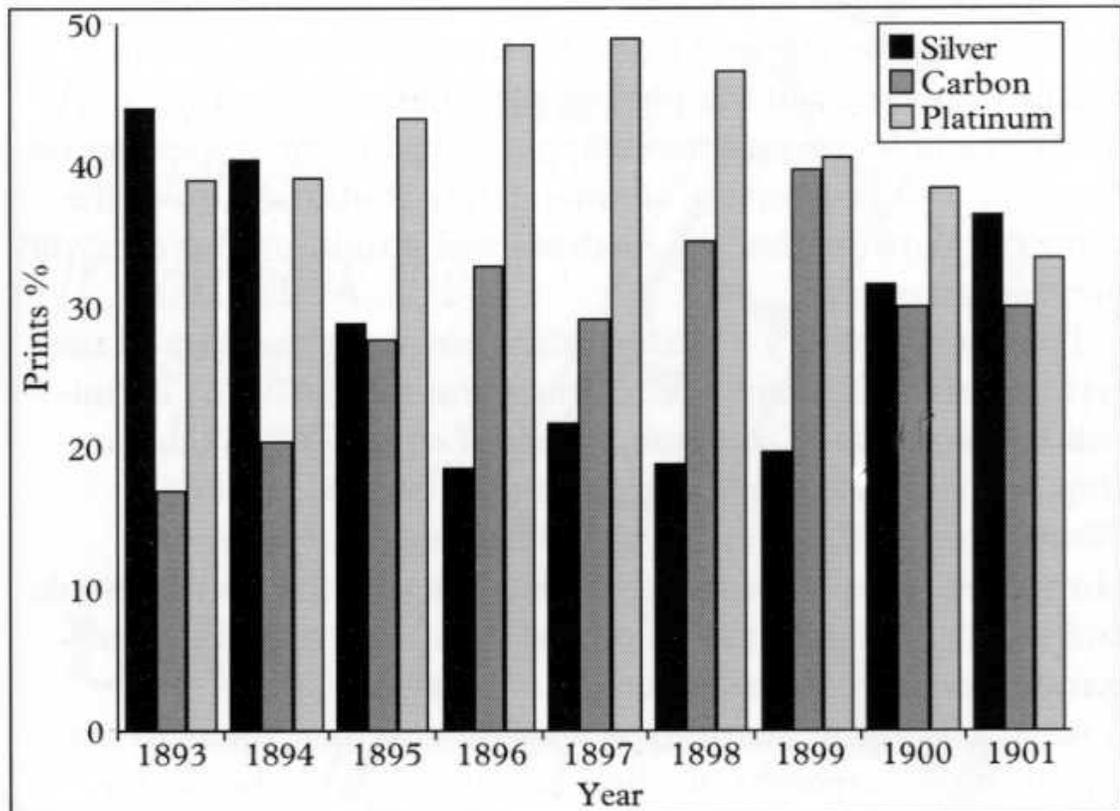


Fig. 1.15 Prints at Royal Photographic Society Exhibitions, 1893–1901 ¹⁷⁶

The aesthetic appeal of the platinotype stems from the integrity of its physical makeup as a 'single layer' print on a sheet of fine, plain paper: the absence of any binder layer, such as albumen, collodion or gelatin, leaves a perfectly matte surface, which is immune to reflective glare under any lighting. The surface displays a lively tactile quality, akin to those other works of art on paper: etchings, engravings, mezzotints, graphite drawings and watercolours. The use of aqueous solutions for the sensitizer, rather than the suspensions of solid particles used for silver-gelatin "emulsions", results in an image composed of platinum nanoparticles lying embedded within the surface fibres of the fine paper sheet, which confers a subtly nuanced neutral grey tonal scale on the image, which cannot be erased without destroying the fibres.

The excellence of a process is reflected in the good opinions of its most distinguished users, so any list of the best-known practitioners of Platinotype must read like a Who's Who of Pictorialism. For instance, Platinotype became the favoured medium of the Brotherhood of the Linked Ring.¹⁷⁷ Notable users

included Frederick Henry Evans (1853–1943), whose great series of cathedral interiors was begun in 1890, printed only in Platinotype; in 1900 his first one-man show at the Royal Photographic Society consisted of 150 Platinotypes. As Anne Hammond has observed:

"Frederick H. Evans remained loyal to the platinum print..."¹⁷⁸

When Platinotype paper later ceased to be made, Evans gave up photography.¹⁷⁹

The most important exhibition work of the leading pictorialist, Henry Peach Robinson (1830–1901), was rendered in Platinotype; in the year of his death his son Ralph printed his father's best images in platinum for public sale.¹⁸⁰ Other notable British works in Platinotype were the portraits by Frederick Hollyer (1837–1933), the atmospheric landscapes of Alfred Horsley Hinton (1863–1908) and George Davison (1854–1930), and the genre studies of Frank Meadow Sutcliffe (1853–1941).

From outside the fraternity of the *Linked Ring*, and frequently in vociferous opposition to it, Peter Henry Emerson (1856–1936), the independently-minded controversialist and critical doyen of art photography, had shown an early enthusiasm for Platinotype. In the autumn of 1882 he submitted four Platinotypes to the 27th Annual Exhibition of the Photographic Society of Great Britain at Pall Mall East, London,¹⁸¹ at a time when only 36 exhibits by eight photographers were in platinum, out of a total of 747 pictures hung by 143 exhibitors.¹⁸² Following this he printed exclusively in platinum, declaring:

"...we emphatically assert that the platinotype process is *facile princeps*." ¹⁸³

To judge by the advice provided by Emerson in his *Naturalistic Photography for Students of the Art*, he did not hand-coat his own paper but recommended Willis's commercial product. 48 of Emerson's platinum prints made during the 1880s are contained in the *Cuba Album*, now in the collection of the George Eastman Museum, which was presented as a gift in 1953 by Dr. William C. Emerson, the nephew of P.H. Emerson (see §9.7).¹⁸⁴ In 1887 Emerson published, with artist Thomas Goodall, their handsome volume of 40 platinotypes, *Life and Landscape on the Norfolk Broads*, which was printed by James Valentine and Sons of Dundee, in a limited edition of 200, 25 of which were embellished with a *de luxe* binding.¹⁸⁵ This volume is now valued as one of the great treasures of the pictorialist canon – a 'standard' copy realised £75,900 at auction in 2013.¹⁸⁶ It is not yet known which paper was used by Valentines for this substantial print run of 8000 platinotypes around 1886, but Clarke's detection of cobalt in the XRF, see §5.5, implies that it contained smalt (a cobalt silicate agent to 'blue' the paper) and probably no lead. Although Emerson's preferred medium for this volume was platinotype, for all his subsequent publications he was obliged to compromise on the expense by adopting photogravure as the closest approach to his ideal.

By the end of the century, the Platinotype process had reached the zenith of its popularity: it was widely acknowledged as the finest printing medium in the entire photographic repertoire. The same Platinotype papers were used in the USA during the first decade of the 20th century by their chief advocate, Alfred Stieglitz (§3.1),¹⁸⁷ the leading light among a group of notable American

photographic artists, especially those of the *Photo-secession Movement* which he founded in 1902, to include Edward Steichen, Frank Eugene, Alvin Langdon Coburn, Clarence H. White, and Gertrude Käsebier. Later, Paul Anderson, Karl Struss, Heinrich Kühn, Frederick Holland Day, Paul Strand and Edward Weston would express similar preferences for the special qualities that platinum could bestow upon their images.

It should not be inferred from this roll-call of the great and good that Platinotype was the exclusive preserve of the photographic luminaries of the day; many examples of Platinotypes produced commercially can be found in ordinary private albums dating from the turn of the century, showing that the medium was also in use for everyday pictorial souvenirs.¹⁸⁸ Advocacy of the Platinotype was not confined solely to the advanced workers, as evinced by publications such as *Photography for Novices* mentioned above in §1.8.

1.13 Book illustrations and artworks

A few high-quality books soon made use of Platinotype for their illustrations: in 1879 an album entitled *Platinotypes of English Cathedrals* was published by Eyre & Spottiswoode,¹⁸⁹ who also later produced a catalogue of paintings photographically reproduced in Platinotype (see below); in the same year another ecclesiastical volume, *The Church of Ireland*, included two Platinotype prints.¹⁹⁰ In 1881 William Willis himself prepared a personal album of travel sketches called *Willis's Pencillings in Wales*, which bore the following explanatory preface, inscribed and signed in his own hand:

“The Pictures in this Book are Photographic Reproductions of Drawings printed in Platinotype and subsequently retouched with crayon by the Artist. The original Drawings were executed with black lead and chalk pencils in the years 1877–78 by W. Willis. Bromley, Kent, July 1881.”¹⁹¹

Less well known is that Willis, evidently an accomplished landscape artist like his father, also published in June 1881 a similar set of 38 platinotypes of his drawings from 1879–80, entitled *Willis's Pencillings in Warwickshire*.¹⁹²

In 1884 Edward Bradbury's popular tourist guidebook, *All about Derbyshire*,¹⁹³ was published in an "extra edition" with twelve bound-in original Platinotype illustrations by Richard Keene of Derby, the leading professional photographer of the County of Derbyshire,¹⁹⁴ who had taken up the Platinotype process for commercial purposes as early as 1879 – for illustrations from this book, see §9.11. Bradbury followed this with another travel volume in 1891, *Pictures of the Peak*, again containing ten Platinotypes by Richard Keene.¹⁹⁵

Platinum was also esteemed as an appropriate medium for reproducing copies of famous works of art. Frederick Hollyer (1837–1933), originally a skilled engraver, became a noted photographic portraitist in his own right, and the leading photographer of works of art. He published many reproductions in platinum, both of old masters and of the work of his contemporaries in the *Pre-Raphaelite Brotherhood*. For example the 1902 *Catalogue of Platinotype Reproductions of Pictures, photographed and sold by Mr. Hollyer*, lists many hundreds of titles of works by artists such as Burne-Jones, Watts, Rossetti and Holbein, which he had photographed himself from various collections.¹⁹⁶

Concerning the appropriateness of the platinotype medium for copying such works, Martin Barnes, present curator of photographs at the V&A, observes:

"With their matt finish, platinum prints rendered the surfaces of pencil or charcoal drawings with great veracity and tonal subtlety. Many of Hollyer's platinum print photographs of drawings are difficult to distinguish from the original..."¹⁹⁷

By 1897, in the USA, Alfred Clements had also assumed the business title of "The London Art Publishers"; an example of their advertisement from 1900 where prints are offered on "Willis & Clements Platinotype paper" may be seen in the Getty Images collection (fig. 1.16).¹⁹⁸

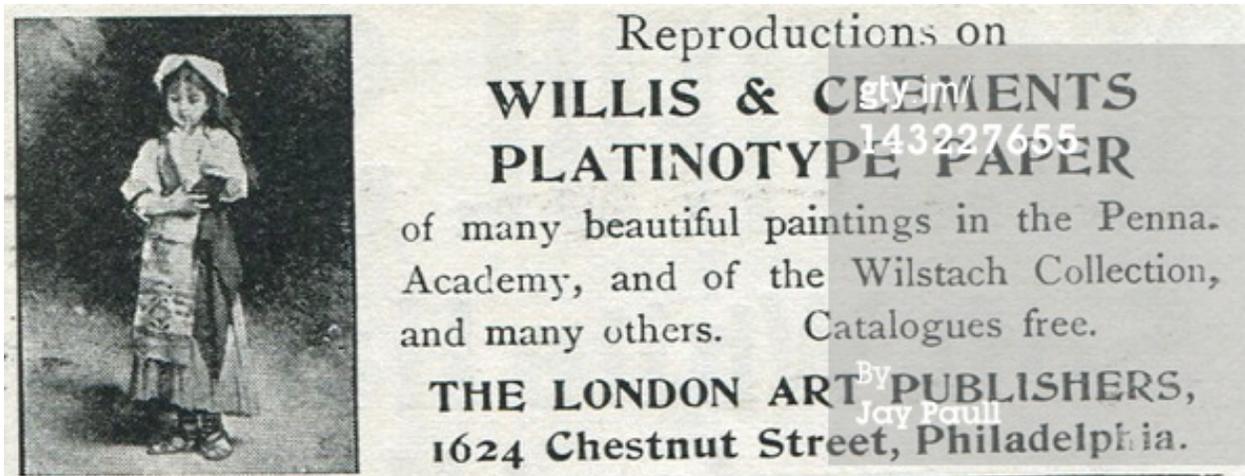


Fig. 1.16 Advertisement for the London Art Publishers featuring Willis & Clements Platinotype paper, 1900. Photo by Jay Paull/Getty Images

They acted as the American agent for, among other artists, Frederick Hollyer's platinotype reproductions of famous art works, as shown in fig. 1.17. As Dr. Carolyn Conroy has explained:

"Hollyer had been advertising the sale of a catalogue of his "Reproductions" in the *Art Amateur* since 1896, which could be obtained in the United States via his American agents "Willis and Clements" of 1624 Chestnut Street, Philadelphia. By 1897, this company had become "The London Art Publishers", although they continued to trade from the same address, and to sell Hollyer's reproductions of Solomon's work, alongside that of Watts, Burne-Jones and Rossetti to an American audience."¹⁹⁹

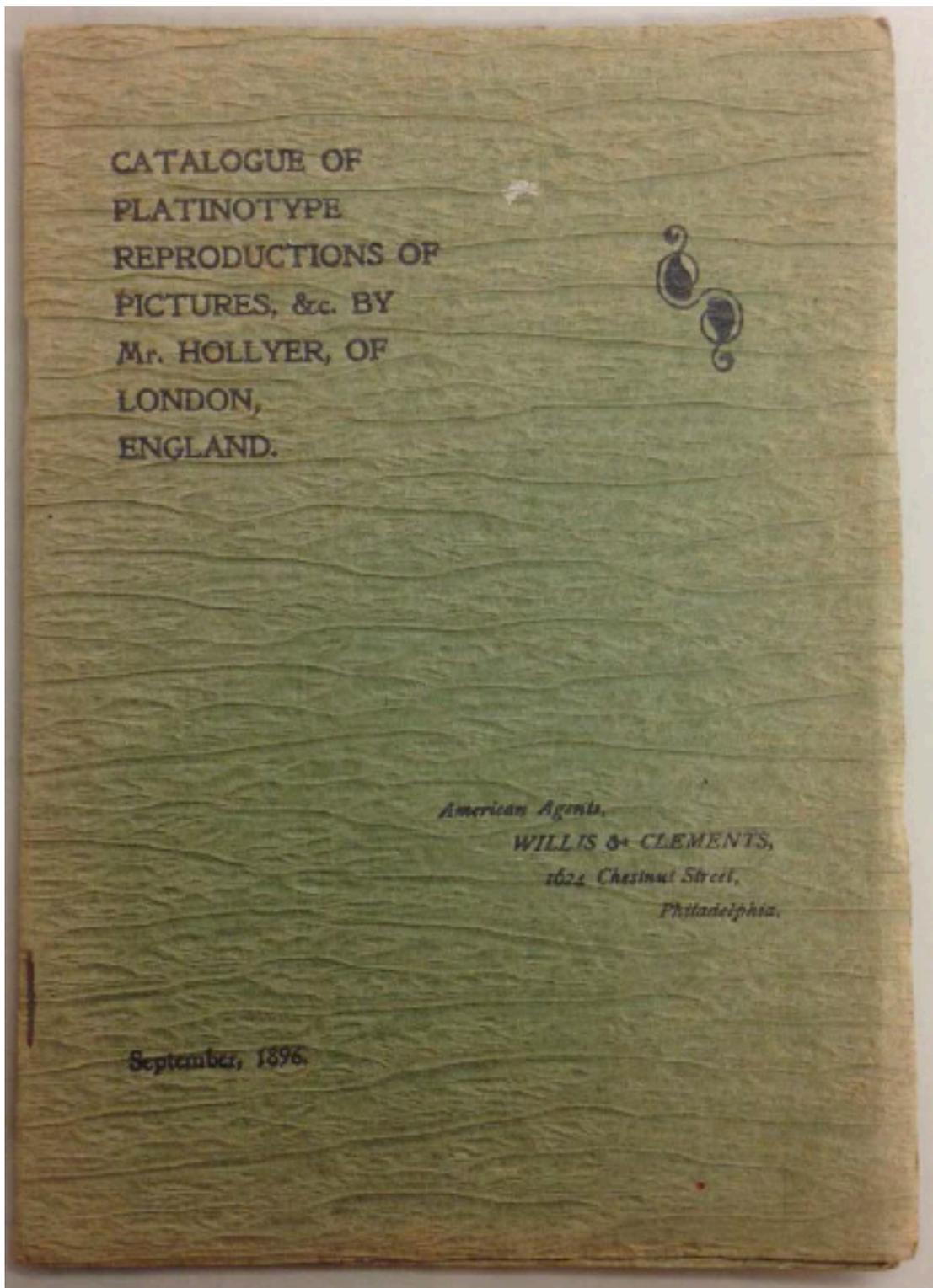


Fig. 1.17 *Catalogue of Platinotype Reproductions of Pictures, &c. by Mr. Hollyer, of London, England. 1896.*

Library of the National Gallery of Art, Washington, DC.

A further tribute to the prestige enjoyed by the platinum print for reprographic purposes is represented by the publication around 1910 by Eyre & Spottiswoode of a *Catalogue of Sepia Platinotype Reproductions of Famous Pictures*, fig. 1.18, which offered some five hundred titles. It is remarkable that the publishers should have found it commercially viable to reproduce, as monochrome sepia Platinotypes, facsimiles of such noted paintings as the *Mona Lisa* or *The Fighting Temeraire*.

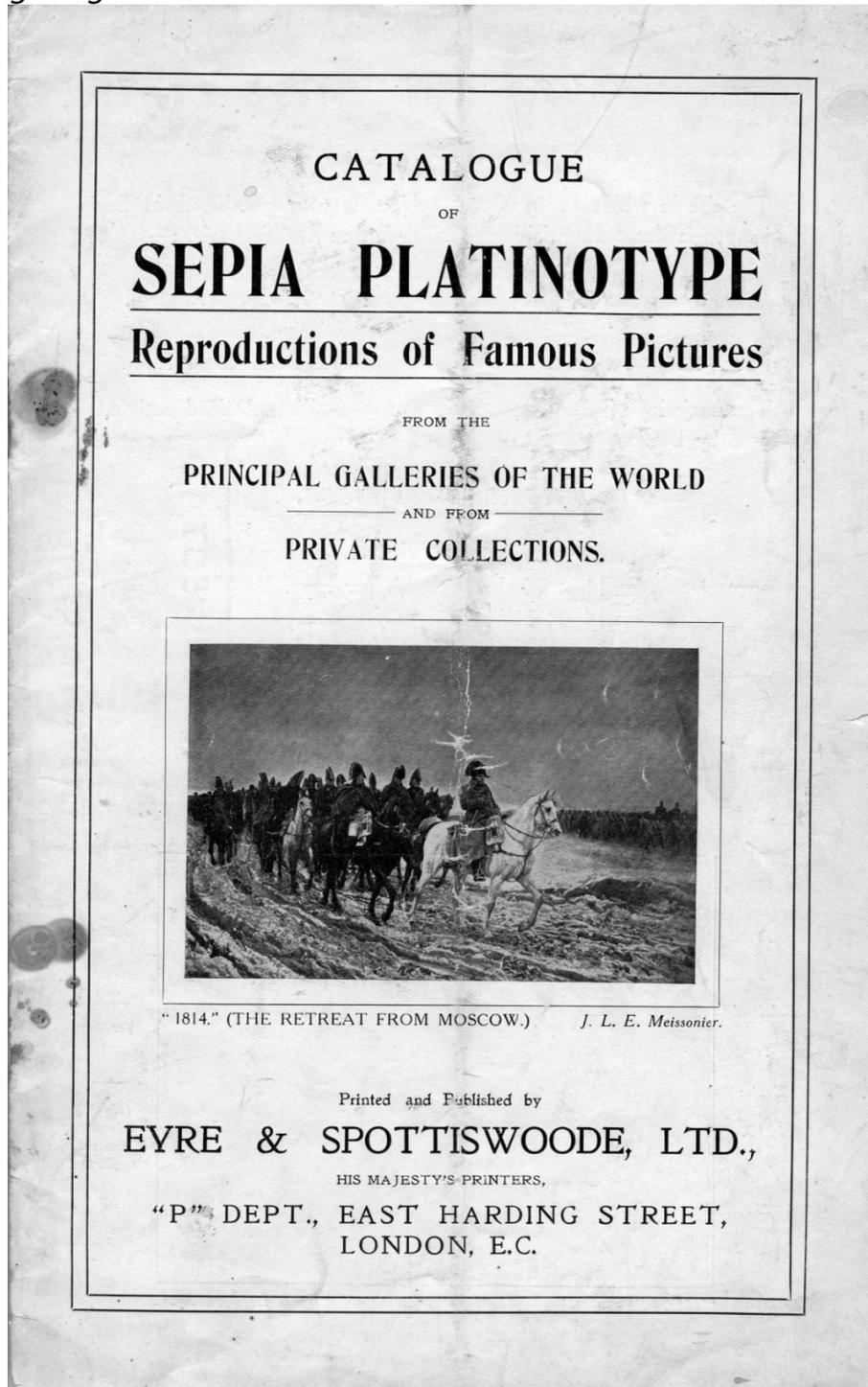


Fig. 1.18 *Catalogue of Sepia Platinotypes of Paintings ca. 1910*

In 1913, Frederick Evans made a number of enlarged photographic reproductions of historic illustrations by well-known artists, and printed them in platinotype for publication in limited editions; these included a set of wood engravings by Hans Holbein;²⁰⁰ some drawings by Aubrey Beardsley;²⁰¹ and in 1919, 17 illustrations by William Blake to the *Pastorals* of Vergil.²⁰²

1.14 Platinotype Company papers and fabrics

An early instruction pamphlet and price list of 1883 by the Platinotype Company of London shows that their papers were initially marketed in three qualities: of medium and heavy weights with a smooth surface, and a heavy weight with a rough surface, in sheet sizes of 17.75 x 22.75 and 24 x 30 inches, at a unit cost of ca. 4.5 d/ft² ("old pence" Sterling per square foot). However, at this time the Company was also offering a surprising variety of cotton and linen fabrics coated with the sensitizer:

"Nainsook (a very fine muslin) gives fine detail and is suitable for prints to be sewn into or on other fabrics. Sateen gives fair detail and is suitable for d'oyleys, mats and transparencies. Oatmeal cloth has a rough artistic surface, very suitable for bold decorative subjects on banner-screens, antimacassars, cosies, mantel-cloths, &c. It gives admirable results."²⁰³

"Linens, jaconette and jean" were also listed, and silks and satins were said to be: "under experiment, and will probably be introduced shortly." However, an examination of subsequent Platinotype Company price lists and instruction booklets does not reveal any further ongoing advertising of sensitized fabrics, which strongly suggests that the Company discontinued this product line at an early stage, ca. 1885. The litany of Victorian parlour accessories quoted above, together with "lamp shades and window screens", leaves one wondering why this use of Platinotype for home decoration should have failed to catch on – especially in view of the extensive use of the similar cyanotype process for embellishing dresses, quilts, cushion covers, upholstery, etc., with photographic illustrations.²⁰⁴ But fabrics tend to absorb much more of the sensitizer per unit area than do well-sized papers; in view of the rising cost of platinum, it seems likely that Willis was unable to reach an economic price that satisfied his clients. Even in 1883, the sensitized fabrics were advertised at about four times the price of the papers: *i.e.* 1/6d or 18 d/ft². A remarkable late (ca. 1911) example of this medium is a platinum print on fabric by Frederick H. Evans of his photograph of an altar cloth from Durham Cathedral.²⁰⁵

By 1892, the Company was offering Platinotype papers only, in nine sizes pre-cut to match the negative formats then current, at a unit cost of ca. 8 d/ft², a price that remained constant over the next 15 years, and may be compared with the price of ca. 3 d/ft² for printing-out papers, and 6 d/ft² for the new bromide enlarging papers.²⁰⁶ The average unit cost may be inferred from the detailed prices given in the Company's definitive list of 1908, which is shown in fig. 1.19. (8 d Sterling was roughly equivalent to 5 cents US.)

The various papers manufactured at different stages of the Platinotype Company's history are summarised in table 1.1, with their surfaces, weights, and image colours. These were allocated alphabetical codes by the Company to indicate what was called the paper "Grade": at first, a single letter designated

the early hot bath papers, of the various weights and surfaces indicated, and later a doubled letter was used for the improved cold development papers which took over after 1892; the letter "S" included in the code always indicated a sepia paper which incorporated a mercury(II) salt in the sensitizer and required hot bath development. Later, after 1906, the code employed the letter "J" to identify the grades of papers with a semi-glossy or "Japine" surface (§1.15), and the letter "B" to designate papers of buff-tinted stock. The paper Grade was usually marked by hand on the label of each tin, and on the cardboard box containing it, together with a batch number or alphabetical code, the paper size, and the number of sheets it contained.

The Platinotype papers on the market during the later years of the 1930s, before the Company's final closure in 1937, are also listed in table 1.1, and are derived from a transcription of the label on a tin of Platinotype paper dated 1936 as shown in table 1.2; these agree exactly with the then current papers listed by Owen Wheeler in his textbook of 1930.²²²

Desiccation of the coated papers before storage was evidently a commercial imperative: only by this means could Willis be confident about the shelf-life of his product, and guarantee its independence of the ambient humidity in greatly differing environments. To this end the Platinotype Company's papers, at some time after 1888, were always packaged in solder-sealed tins (fig. 1.20.) containing a sachet of desiccant, which was anhydrous calcium chloride dispersed over asbestos wool, so could be regenerated by strong heat. It was always recommended that, on cutting the tin open, the entire contents of paper should be immediately transferred to a 'calcium chloride storage cylinder' specially manufactured by the Platinotype Company for this purpose.²⁰⁷ Even so, users were recommended by the Company not to buy a greater stock of paper than could be used up in "a month or so".²⁰⁸ It appears from the following exchange at a Society meeting in 1887 that even the precaution of desiccated storage did not guarantee the quality of the paper for very long:

"Mr. HENDERSON asked how long the paper would keep in good condition if kept perfectly dry all the time.

Mr. WILLIS replied that that was an unknown quantity, but he could say with almost absolute certainty that it would keep good for two months. Sometimes paper a year old proved to be as good as new, but, as a general rule, he gave two months as the life of the paper, even when kept all the time in a tube with chloride of calcium." ²⁰⁹

However by 1891 Willis had evidently gained a good deal more confidence in the longevity of his product, and extended his claim for its stability from two months to six, or possibly more:

"I have seen excellent prints made on paper eighteen months old, and which had been round the world. I have seen paper two years old which was in very fair condition. I had some paper developed which was six years old, but the whites were degraded. ...the life of the paper is now at least six months... I think sepia paper keeps if anything better than the other." ²¹⁰

Table 1.1 Dates and Descriptions of Platinotype Company Papers.

NB: All are platinum, except where indicated in column 5.
 Dates indicate earliest known reference found, not timelines of use.
 All the "black" Pt papers could also be "sepia developed" by adding the Company's proprietary "Special Sepia Solution" to the oxalate developer.

Year & Ref. no.	Grade or Name	Paper Weight	Surface Texture	Colour and Development
1879 ²¹¹	None	Medium	Smooth	Black, Hot bath
	None	Heavy	Rough	Black, Hot bath
1883 ²¹²	None	Heavy	Smooth	Black, Hot bath
1888 ²¹³	Cold bath: All of the platinum salt in developer bath: its very poor keeping qualities were uneconomic. Willis suspended licence fee			
1892 ²¹⁴	A	Medium	Smooth	Black, Hot bath
	B	Heavy	Smooth	Black, Hot bath
	C	Very heavy	Rough	Black, Hot bath
	S	Medium	Smooth	Sepia, Hot bath
1892 ²¹⁵	X Cold development: Platinum salt in sensitized paper. No patent Grade X was soon replaced in 1893 by the following system:			
1893 ²¹⁶ 1896 ²¹⁷	AA	Medium rel. value 1	Smooth	Black, Cold bath
	BB	Heavy	Smooth	Black, Cold bath Discontinued c.1904
	CC	Very heavy	Rough	Black, Cold bath
	S	Medium	Smooth	Sepia, Hot bath
	RS	Very heavy	Rough	Sepia, Hot bath
1902 ²¹⁸	KK	Heavy rel value 1.75	Smooth	Black, Cold bath Higher Contrast
1902 ²¹⁹	TT	Heavy rel value 1.75	Rough	Black, Cold bath Higher Contrast
1906 ²²⁰	Japine Sepia	Medium	Extra Smooth Semi-glossy and Matt	Sepia, Hot bath Parchmentized surface
1908 ²²¹	Japine black	Medium	Extra Smooth Semi-glossy and Matt	Black, Cold bath Parchmentized surface

Table 1.1 Continued...

Table 1.1 Dates and Descriptions of Platinotype Company Papers. *Contd.*

Year & Ref. no.	Grade or Name	Paper Weight	Surface Texture	Colour and Development
1908 ²²²	The Platinotype Company's Revised List has the following black papers for "cold development", and Sepia papers for "hot bath":			
	AA	Medium rel. value 1	Smooth	Black, Cold bath
	CC	Extra heavy	Rough	Black, Cold bath
	KK	Heavy rel value 1.75	Smooth	Black, Cold bath Higher contrast
	TT	Heavy rel value 1.75	Rough	Black, Cold bath Higher contrast
	YY	Extra heavy rel value 2.5	Smooth	Black, Cold bath
	ZZ	Extra heavy rel value 2.5	Slightly rough	Black, Cold bath
	Japine KK	Heavy	Very smooth Semi-glossy	Black, Cold bath Parchmentized
	Japine YY	Extra heavy	Very smooth Semi-glossy	Black, Cold bath Parchmentized
	KS	Medium	Smooth	Sepia, Hot bath
	RS	Extra heavy	Rough	Sepia, Hot bath
	TS	Heavy	Rough	Sepia, Hot bath
	YS	Extra heavy	Smooth	Sepia, Hot bath
	ZS	Extra heavy	Slightly rough	Sepia, Hot bath
1911 ²²³	Japine Sepia Buff		Very smooth	Buff paper stock Sepia, Hot bath
	Sepia Buff		Matt	Sepia, Hot bath
	Buff stock		Matt	Black, Cold bath
1912 ²²⁴	Ivory black		Smooth and Rough	Warm black, special hot developer
1913 ²²⁵	Satista		Smooth	Silver + platinum Black and Sepia
1916 ²²⁶	Satistoid later Satoid	3 weights	Smooth and Rough	Silver + platinum Brown Name changed

Table 1.1 Continued...

Table 1.1 Dates and Descriptions of Platinotype Company Papers. *Contd.*

Year & Ref. no.	Grade or Name	Paper Weight	Surface Texture	Colour and Development
1916 ²²⁷	Sepia Japine K	Heavy	Smooth	Sepia, hot bath White stock
	Sepia Japine Y	Extra heavy	Smooth	Sepia, hot bath White and buff stock
1915 ²²⁸	Japine Silver		Vellum	Silver printout paper Brown to warm black
1917 ²²⁹	Palladio-type		Japine	Palladium paper Brown No patent
1918 ²³⁰	Palladio-type BM		Smooth Matt	Palladium paper Warm black on white stock and buff stock
1920 ²³¹	Satista Buff		Smooth Buff	Silver + platinum Black and Sepia
1930 ²³² 1936 ²³³	A few years before it closed the Company was offering 12 papers: AA, CC, KK, YY, KS, YS, as 1908, above. Additionally there were:			
	BS	Heavy	Smooth	Sepia on Buff stock
	CS	Heavy	Rough	Sepia, Hot bath
	KJ	Heavy	Smooth	Black Japine
	KJS	Heavy	Smooth	Sepia Japine
	CJB	Heavy	Smooth	Black Japine on Buff
	BJS	Heavy	Smooth	Sepia Japine on Buff
ca. 1931	"WBJ"	Heavy	Smooth	"Warm Black Japine" Special extra coating for Paul Strand et al.

Table 1.1

Revised Price List of . . .

PLATINOTYPE PAPER.

	AA, KK, CC, TT.	YY, ZZ.	KS, RS, TS, Japine.	YS, ZS.	Post- age.
	<i>s. d.</i>	<i>s. d.</i>	<i>s. d.</i>	<i>s. d.</i>	<i>d.</i>
$\frac{1}{4}$ plate, per tube of 24 pieces	1 8	1 10	2 0	2 3	3
5 × 4 " " " " "	2 4	2 6	2 8	3 0	3
6 × 4 $\frac{1}{4}$ " " " " "	3 0	3 3	3 4	3 8	3
$\frac{1}{2}$ plate " " " " "	3 6	3 10	4 0	4 5	3
7 $\frac{1}{2}$ × 5 " " " " "	4 4	4 9	5 0	5 6	3
1/1 plate " " " " "	6 6	7 1	7 2	8 0	3
10 × 8 " " " 12 "	4 8	5 2	5 3	5 10	3
12 × 10 " " " " "	7 0	7 9	7 10	8 8	3
15 × 12 " " " " "	10 4	11 3	11 9	12 11	4
1 Sheet 26 × 20	3 0	3 3	3 4	3 8	4
3 " "	8 0	8 9	9 0	10 0	4
6 " "	15 6	17 0	17 6	19 3	4
12 " "	30 0	33 0	34 0	37 6	5
24 " "	60 0	66 0	68 0	75 0	7

Postcards :

Pkt. of 8, with Developing Salts, Acid & 2 Masks	<i>s. d.</i>	<i>d.</i>
Per tube of 1 dozen	1 6	Postage 3
 1 6 " 3

NOTE—All previous lists, quotations, etc., are hereby cancelled.

THE PLATINOTYPE COMPANY,
22, BLOOMSBURY STREET,
NEW OXFORD STREET, LONDON, W.C.

1st June, 1908.

Fig. 1.19 Official Price list of Platinotype Company papers 1908

Platinotype papers

AA	For the Cold-Bath Process	Smooth Paper. Medium thickness.
KK	do. do.	Smooth thick Paper, fine surface gives very bright prints.
CC	do. do.	Rough-surfaced Paper. Thick and very strong.
YY	do. do.	Very thick smooth Paper
KS	For the Hot-Bath Process	Smooth Paper. To give rich Sepia colour
BS	do. do.	Thick smooth buff-tinted Paper for Sepia
CS	do. do.	Thick rough surface Paper for Sepia
YS	do. do.	Extra-thick smooth Paper for Sepia
BLACK JAPINE)	
SEPIA JAPINE)	Semi-matt surface
BUFF SEPIA JAPINE)	
CREAM WARM-BLACK JAPINE)	

Table 1.2 Transcript from label of a tin of 'KK' Platinotype paper 1936
Collection of the Museum of the History of Science, Oxford ²³⁴

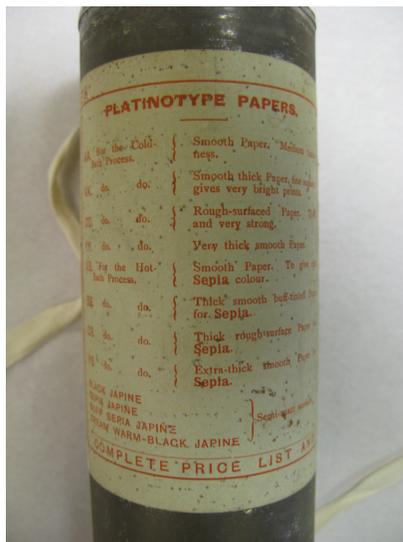




Fig. 1.20 Typical tins of commercial Platinotype paper ca. 1906
 Photograph courtesy of Constance McCabe. The tin of Grade 'AA' paper, lower left, is the generous donation of Mr. Robert F. White of the PCCGB.

Other goods marketed by the Platinotype Company included relevant chemicals, porcelain dishes, printing frames, and storage tubes desiccated with calcium chloride. Willis's co-director of the Company, Herbert Bowyer Berkeley (1851–1891), was also responsible for discovering one of the most significant improvements in processing photographic negatives: that developers for silver emulsions could be stabilized by the inclusion of sodium sulphite, which enabled the development of camera negatives to greater density ranges without fogging, so providing a better match to the long exposure scale of the platinotype process. The Company marketed this important innovation in 1882 as the very first proprietary developer, "Sulpho-pyrogallol".²³⁵ The works manager of the Company's factory in Penge, W.H. Smith, collaborated with Willis to produce a hand-portable "Key camera", patented on 28 March 1889, which incorporated a novel method of changing the glass plates. For a short time only – perhaps not surprisingly – the Company also marketed, for two guineas, a fearsome "Platinotype printing lamp" in which magnesium powder was driven by a stream of compressed hydrogen gas, meeting a stream of oxygen gas, also under pressure, at the jet of the burner, to provide a "flame of intense actinic power" which sufficed to expose platinotypes "in a few seconds".²³⁶ It is unlikely that such a light source would be welcomed today by the Health & Safety Executive.

Around 1900, the pure chemical, potassium chloroplatinite, was marketed chiefly by the leading British precious-metal refiners, the Johnson Matthey Company, who sold it to Willis for the manufacture of Platinotype paper. The sales figures for this product have been discovered in the Johnson Matthey Company records by Ian Cottington, and his figures show that the sales curve passed through a peak in 1905, fig. 1.21.²³⁷

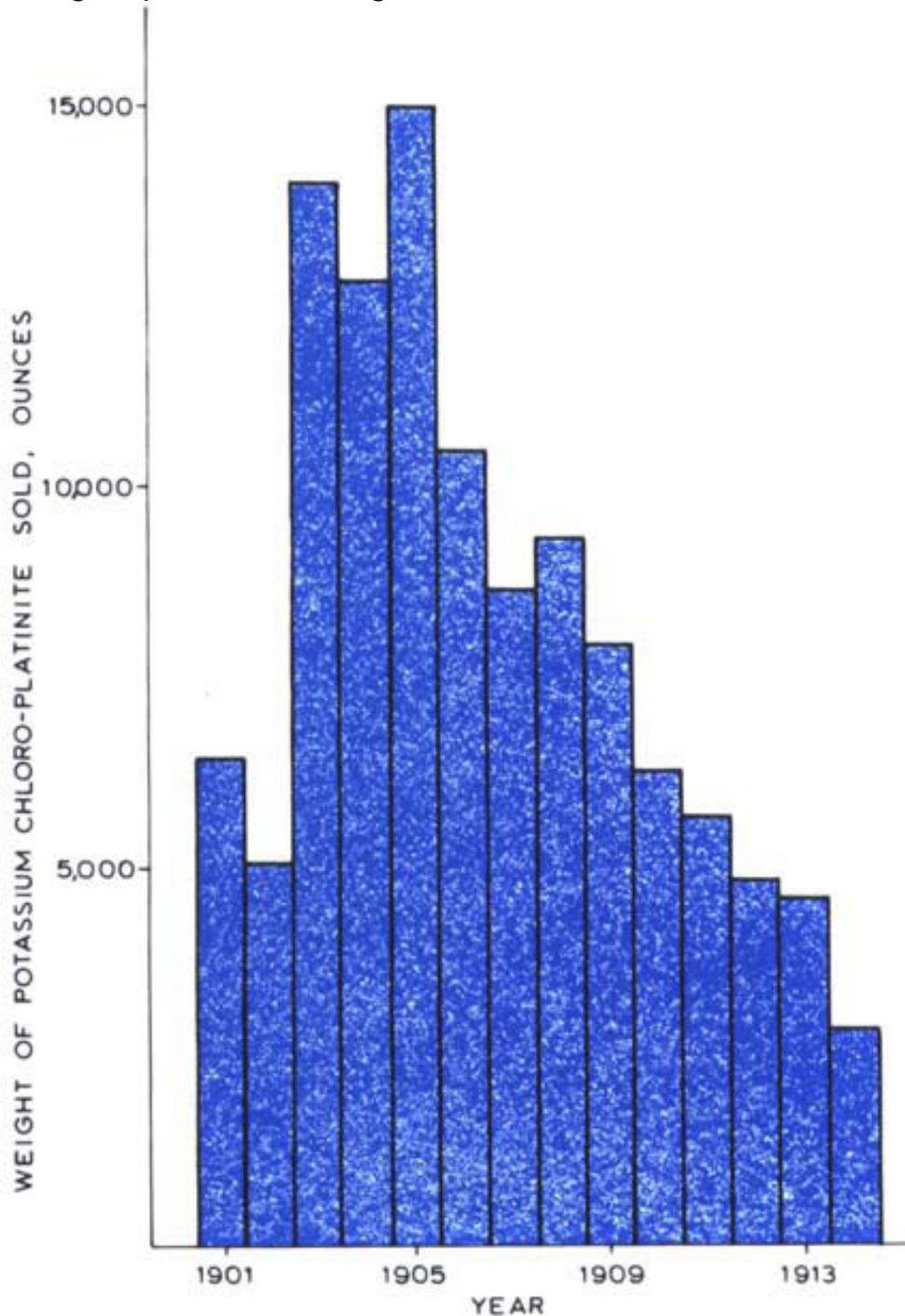


Fig. 1.21 Sales by Johnson Matthey of Potassium Chloroplatinite 1901-14

(Courtesy of Ian Cottington, Johnson Matthey Co. Ltd.)

From these data we can calculate that, over the years 1901 to 1914, the total quantity of potassium chloroplatinite sold (presumably most of it to Willis's Platinotype Company, for it had no other uses) amounted to about 113,600 Troy ounces. This figure provides the basis for a simple but instructive estimate of the Platinotype Company's output: we know from his patent specifications that Willis's Platinotype paper had, at most, a coating weight of 4 grains of this substance per square foot (§5.1). There are 480 grains in a Troy ounce. The area of Platinotype paper manufactured during these 14 years is hence easily calculated; the average annual production of platinotype paper was usually in excess of one million square feet.²³⁸ This result may be vividly expressed in terms of the total number of 'whole plate' prints which this area could produce over the 14 years of platinotype hey-day: the number is about 35 million! Considering the limited extent of the platinotype holdings of our major collections, we may conclude that either there are many historic platinotypes still 'out there' to be discovered, or else that the process was more fallible than it is usually represented, and much spoiled paper ended up in the wastebin! Whichever is the case, the consumption of material attests to its popularity.

1.15 Willis's "Japine" papers

The so-named Japine papers were launched in 1906,² heralded by a considerable advertising fanfare (fig. 1.22);²³⁹ they differed from the matt finish of all Willis's previous papers in displaying a semi-gloss or 'egg-shell' surface quality, with a distinct sheen. Initially they were available only as sepia toned papers, but in 1908 a "black" version was also marketed.²⁴⁰ The origin of this surface texture and its exact nature is a question originally raised by Lisa Barro in 2002, relating to her studies of conserving the work of Paul Strand in this medium.²⁴¹ She pointed out that there is written evidence that Willis's Japine Platinotype papers may have been coated onto stock that had been partially 'parchmentized'.²⁴² This is a process that typically involves a brief (3–10 seconds) treatment with strong (65–75%) sulphuric acid, followed by thorough washing and neutralising with alkali (usually soda).²⁴³

² *Etymological footnote 2: The word "Japine" appears to have been invented by Willis himself ca. 1906; we can find no record of it prior to his advertisements which launched his "Japine Platinotype paper", fig. 1.15. The word "Japine" is not in the Oxford English Dictionary, and is not known to paper historians or conservators. Willis may have derived it from the contemporary fine papers designated in French as 'simili Japon' by their makers because they mimicked the expensive handmade papers of Japan. Even the font chosen for the lettering on the paper tin's label initially affected an 'oriental' style. Things Japanese were highly fashionable in England in the first decade of the 20th century, and "japanese tissue" was popular for printmaking.*

<p>THE PLATINOTYPE The leading Photographers of England have been converted to JAPINE <i>Send for sample print, instructions, etc.</i></p>	<p>WILLIS & CLEMENTS PHILADELPHIA PENNSYLVANIA</p>
---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------	------------------------------------------------------------------------------------------------------------

x THE AMATEUR PHOTOGRAPHER ADVERTISEMENTS. January 21, 1908.

Have you tried the
 New Japine Paper?
 It is splendid.

THE PLATINOTYPE CO.,
 22, Bloomsbury Street,
 New Oxford Street, W.C.

PLEASE MENTION THIS JOURNAL WHEN CORRESPONDING WITH ADVERTISERS.

xiv THE AMATEUR PHOTOGRAPHER ADVERTISEMENTS. August 21, 1906.

What the *Morning Post* says about
**JAPINE
 PLATINOTYPE.**

Probably the 1906 Convention will be best remembered as the occasion when the new Platinotype paper known as "Japine" was introduced to the photographic world. The paper in question provides what many amateurs have been intensely longing for, *i.e.*, a sepia brown Platinum print, which, instead of having a dull surface, should possess the half glossy "egg shell" surface met with in some carbon prints. Platinotype workers have often wished that the same effect which was apparent as the wet print lay in the developer could be retained by the dry print. This, in a large measure, is what the Japine paper effects, the shadows being not dull, but rich and lustrous. Moreover, the range of gradation has been considerably augmented, as I have been able to assure myself by a careful comparison of prints taken on the old and the new papers. When it is added that the printing latitude of Japine is twice as great as that of ordinary Platinotype, and that its damp-resisting power is tenfold as great, it will be realised that there is likely to be a considerable popularity for this notable improvement of variation in Platinotype printing.

**Sold in Semi-matt or Glossy Surfaces, at
 same prices as our ordinary papers.**

HOT OR COLD DEVELOPMENT.

**THE PLATINOTYPE COMPANY,
 22, BLOOMSBURY STREET, LONDON, W.C.**

PLEASE MENTION THIS JOURNAL WHEN CORRESPONDING WITH ADVERTISERS.

Fig. 1.22 Platinotype Company advertisements for "Japine" paper 1906/8

In his "Satista" patent of 1913, Willis indicated that such a paper was a possible substrate:

"I have further found that particularly advantageous results can be obtained in the above process by using paper the surface of which has been parchmented by treatment with acid or by other well known means. The paper is coated or treated on each side with sulphuric acid sufficiently strong to attack the paper; the paper is well washed in water to free it from acid and is then dried. The acid is not left on long enough to penetrate the paper, the aim being to get a film of altered paper on each side."²⁴⁴

but Willis does not there use the word "Japine". However, the *British Journal Photographic Almanac* stated that:

"... of the two grades of 'Satista', black and sepia, both were coated on semi-matt hard-surfaced paper similar to Japine."²⁴⁵

and in 1915 a visitor to the Platinotype Company's factory at Penge stated that 'Satista' had indeed been coated on Japine paper hitherto, and now welcomed the fact that:

"...the process has been adapted to the other papers and surfaces. This will undoubtedly add immensely to the popularity of "Satista" ..." ²⁴⁶

The Technical Manager of Willis's Platinotype Company, William H. Smith, also described a Japine silver paper to the Royal Photographic Society in these terms:

"...in this case there is no gelatine or anything that can rub off the paper or that can be affected by hot water, and the paper will stand almost any amount of rubbing without fear of abrasion." ²⁴⁷

Furthermore, Willis's long term employee, Ernest A. Salt, described the paper in 1929 thus:

"..."Japine" Platinotypes, which present a semi-matt surface. This is not an applied coating but is integral with the paper." ²⁴⁸

The same explanation was given by Owen Wheeler, in his text of 1930:

"... [Japine] is not a coating, but exists as an integral part of the paper itself, giving maximum detail and shadow transparency." ²⁴⁹

It has been a recent research objective to identify platinum and palladium prints of this "Japine" type in order to determine its nature, and possibly simulate it with modern "vegetable parchment" papers, which emulate the qualities of vellum and parchment skins.²⁵⁰ There has recently been an in-depth scientific investigation of Japine Platinotype papers at the National Gallery of Art, Washington, and the Metropolitan Museum of Art, New York, whose scientific teams have confirmed the speculations entertained above, and have succeeded in simulating the Japine surface and printing on it in platinum and palladium, as will be described in §5.7.²⁵¹ A tin of "Black japine platinum paper" owned by photographer Rob McElroy,²⁵² was recently opened by Professor Patrick Ravines, and the process and analysis were recorded. An unopened sealed tin of unexposed paper described as "Warm-Black Japine Platinotype", Grade CJB, dated 1936, is held in the collection of the Museum of the History of Science in Oxford.²⁵³

1.16 Researches of Pizzighelli and Hübl

Writers on Platinotype, in its early days in Britain, seem to have been careful not to provide explicit instructions on how to prepare the sensitized paper, probably for fear of infringing Willis's patent rights. However, in 1882 two Austrian army captains in the photographic department of the military technical administration, Giuseppe Pizzighelli (1849–1912) and Baron Arthur von Hübl (1853–1932), were the first to publish detailed recipes and instructions, in German, for their version of platinum printing, for the benefit of practitioners who were prepared to mix their own chemical solutions and hand-coat their own papers.²⁵⁴ The sensitizer was based on ferric oxalate, with optional

contrast enhancement by a variable amount of potassium chlorate. A conventional developer of hot potassium oxalate solution was needed.

The Vienna Photographic Society awarded its Voigtländer Prize to this publication, which was soon translated from German into both French,²⁵⁵ and English and published in the British photographic press in 1883.²⁵⁶ This publication opened up the technique by making practical details and formulae generally accessible to all, and may have been responsible for the emergence of some commercial competition to Willis's erstwhile monopoly.

In 1887, Pizzighelli, by then working alone in Benjaluka, Bosnia, made a significant addition to the canon: he discovered an alternative iron sensitizer formulation that yielded a printed-out platinum image directly on exposure, needing no developer, only washing in dilute hydrochloric acid to clear the image.²⁵⁷ The key to this "direct printing platinotype" process, as it was then called,²⁵⁸ was the use of the "double salt" sodium ferric oxalate for the sensitizer, rather than ferric oxalate (for an explanation of the photochemistry see §11.2, and for detailed formulations see §5.3). Pizzighelli also described the results of testing ammonium ferric oxalate:

"Of the double salts experimented with, the sodium-ferric oxalate proved the most satisfactory, the corresponding potassium salt giving less sensitiveness; while the ammonium salt, although giving greater sensitiveness, gives less brilliant images than the sodium salt, and, moreover, images having a tendency to a cold, bluish tone."²⁵⁹

The substance of this German discovery was quickly translated and relayed to the English-speaking readership of *The Amateur Photographer* by Alfred Stieglitz, then resident in Germany (§3.1).²⁶⁰ These "double salts" were not, however, new: there was a long-standing precedent in siderotype photography for the use of sodium or ammonium ferric oxalate as alternatives to ferric oxalate as sensitizer.²⁶¹ Hermann Halleur had described the use of ammonium ferric oxalate to make silver prints as early as 1853,²⁶² and Charles Burnett (§1.4) and John Mercer were separately using it by 1858. It was advocated for the cyanotype process by Carey Lea in 1863,²⁶³ and later by Traill-Taylor in 1889,²⁶⁴ but created problems of crystallization with this process which were only solved much later.²⁶⁵ Pizzighelli's "direct printing" or "water developed" platinotype formulation was similar in its concentrations of iron and platinum salts to the development process (§5.3), and it was taken up commercially by a number of manufacturers (see §1.17) but, after an initial flush of enthusiasm, these papers did not remain on the market for very long, possibly for reasons of limited storage life and the need for control of the humidity in their use.

In 1895 the leading British photographic scientist, William de Wivelesley Abney, and Lyonel Clark, published their treatise, *Platinotype: its Preparation and Manipulation*, which provided an historical review and gave practical details of formulae for hand-coating papers.²⁶⁶ In the same year, Baron Arthur von Hübl published, in German, his comprehensive practical handbook, *Der Platindruck*.²⁶⁷ He followed it with a second edition in 1902, where the author indicated in his preface the new developments of recent years:

" During the last few years the theoretical views of the creation and nature of the black platinum image have not changed, and the procedures for making platinum prints have held as well.

All sections concerning the platinum print have not been changed for the second edition except for a few places where an attempt has been made to organize the material better.

The sepia-platinum process had to be completely reworked, since definitive experiments have resulted in new unexpected conclusions on the nature of mercury-platinum prints; these experiments showed the way to achieving prints through the use of cold development.

The theoretical and practical description of the cold-development methods for sepia prints contributes to an enrichment of the contents of the second edition.

Vienna, February 1902." ²⁶⁸

This notable treatise has, regrettably, remained untranslated, other than a selective four-part digest by E.J. Wall which appeared in the *British Journal of Photography* in 1902.²⁶⁹ Other important works published only in German were Joseph Maria Eder's *Lichtpausverfahren die Platinotypie*,²⁷⁰ and the handbooks by J. Gaedicke,²⁷¹ Felix Naumann,²⁷² and Th Romanesco.²⁷³ There were also texts in French by H. Émery (1902) and Eugène Trutat (1904).²⁷⁴

1.17 Other commercial platinum papers

With the publication towards the end of the 19th century of working formulae for platinotype, a number of rival manufacturers surfaced in the market, offering pre-coated platinum papers, although all these business enterprises survived only for much shorter timespans than the Platinotype Company.²⁷⁵ In 1895 the Autotype Company of London, already noted for its range of carbon process papers, was offering a "permanent platinum printing paper" in three varieties: cold bath rough and smooth (C.B.R and C.B.S) and hot bath smooth (H.B.S.); all three were developed in potassium oxalate plus potassium hydrogen phosphate. In 1899 a platinum paper called "Platona" was launched on the market by The Britannia Works Company Limited, the firm that in 1902 was to become the major British photographic materials supplier, Ilford Limited of London.²⁷⁶ This paper was available in two surfaces, and retailed in a tin with an air-tight screw lid. The processing instructions resembled those of the Platinotype Company.²⁷⁷ The Ilford paper remained available at least until 1908. Print-out platinum papers were also offered in Britain by Hardcastle & Co., "photographic chymists" of Brighton; they were described as requiring no development, only clearing in hydrochloric acid.

In Berlin ca. 1890–1906, Drs. Adolf Hesekei & Jacoby were also producing commercial platinum papers, including Dr. Jacoby's "Pizzitype" paper of 1887, a platinum printing-out paper, which was also retailed by Dr. Just in Vienna, and Unger & Hoffmann in Dresden. Dr. Jacoby's paper was imported and retailed in Britain by Otto Schölzig of Clapham and C.A. Rudowsky of London.²⁷⁸ Dr Hesekei's Platina Direct Printing "Pizzighelli" paper was "steam-developed".²⁷⁹ For further information on the German literature and producers of platinum and palladium papers in Germany and Austria, the reader is referred to the article by Andreas Gruber.²⁸⁰

In the USA, several competitors to Willis & Clements emerged: J.C. Millen of Denver, Colorado; the Columbia Photo Co.; E. & H.T. Anthony & Co. of New York; and Joseph Di Nunzio of Boston, who marketed "Angelo" platinum paper from 1906–1915. The Eastman Kodak Company purchased Joseph Di Nunzio of Boston in 1906, and marketed platinum papers through their subsidiary, the American Aristotype Company.²⁸¹ The "American Platinum papers" from the Aristotype Company were available in three weights and two surfaces over the period 1901–1916. But in Britain it was advertised as "Kodak" platinum paper, from their London address. Their products included "Eastman's W.D. (Water Development) paper" (1901–1909) which was presumably of the same type as Dr. Jacoby's "Pizzitype" paper mentioned above. Later Eastman Kodak brought out "Eastman E.B." (Etching Black) and "Eastman E.S." (Etching Sepia) platinum papers (1909–1916).

By 1913 platinum printing was being acknowledged as the "most generally useful process" of photographic printing.²⁸² Its virtue of permanence was also picturesquely extolled by the English photographic chemist, Chapman Jones:

"Thus the platinum image is not only able to resist all detrimental atmospheric influence, but there is no method known by which it can be attacked. As the sensitive substance is put directly upon the paper, the paper must be of excellent quality, free from extraneous matter and fibres of inferior quality, for if any such matters were present they would affect the process and show flaws in the print. The suitability of the paper is therefore a practical guarantee of its purity, and as we know that linen will last for thousands of years, as demonstrated for example in the present condition of the cloths on mummies, there seems every reason to suppose that if platinum prints had been made in Abraham's time, or when Egypt was at the height of its glory, they might, if preserved with reasonable care, have been available for our information at the present day." ²⁸³

A somewhat ironic coda was added to this eulogy in 1929 by E.A. Salt of the Platinotype company:

"Without wishing to introduce any theological questions, I may add they would certainly have survived the flood, for some years ago when a sunken battleship was raised, which had been submerged for 12 months, some Platinotype prints were found in a cabin none the worse for their prolonged immersion in the sea water, though the mounts had disappeared. The prints were subsequently shown at the Brussels Exhibition, and were, unfortunately, destroyed in the fire that occurred there." ²⁸⁴

1.18 "Faux platinum" silver papers

The 3rd edition of the book *Photography for Novices* (1902), previously mentioned in §1.8, carries a frontispiece displaying a plate purportedly printed on "Original Barnet Platino–matt paper", but sadly there can be no platinum in it because the plate is now badly faded and mirrored – which would not have occurred had it been a genuine platinum print. This is an example of the popular market phenomenon that arose ca. 1895, when many photographic paper manufacturers of the day misappropriated the "platinum" name, applying the term "platino–" to their commercial silver–gelatin and silver–collodion

papers that sought to mimic the 'platinum look' by using emulsions to which constituents had been added to suppress the natural glossiness of the surface. Photograph Conservator at the NGA, Sarah Wagner, has appropriately termed these papers as *faux platinum* in her highly detailed account of their manufacturing history:²⁸⁵

"Many *faux platinum* silver products, designed to mimic platinum, were rushed to market with names such as Aristo-Platino, Platino Bromide, Platino Matte Surface (abbreviated to PMS), Platitone, Platinoid, Platino Matt, etc.

As a plain-paper process, platinum had an obvious advantage in the competition for matte-surfaced products. *Faux platinum* papers, with their traditional gelatin and collodion binders, required modification to achieve a similar surface by avoiding highly calendered paper supports, adopting textured baryta layers, using very thin or no baryta, and/or adding matting agents to the binder such as starch and silica."^{286, 287}

It is said that "imitation is the sincerest form of flattery", and these *faux platinum* papers do indeed pay homage to the high aesthetic qualities always attributed to the Platinotype; however, their lack of its long-term archival stability eventually demonstrates the misleading futility of the product names. As a more stable compromise, the so-called "Aristo Platino paper" was a popular silver-collodion paper that was actually toned at the conclusion of its processing in gold or platinum – or preferably both – depending on the hue required.²⁸⁸ Fig. 9.4 in §9.8. shows a labelled example which evidently contains platinum because the image has offset as a brownish positive onto the facing tissue guard sheet – an instance of the phenomenon of "autoplating" (§9.8).

2. Transition from Platinum to Palladium

Rather belatedly, Platinotype eventually rose to pre-eminence as the finest printing medium in the entire photographic repertoire, but this status was short-lived: within 25 years it abruptly fell from popular use. One of the ironies of science is that blame for the premature decline of the Platinotype can be laid at the same door that enabled its rise in the first place – namely, the advance of chemical knowledge. While the discovery of catalysis by platinum heralded a profitable revolution for the chemical industry, it also sounded the death knell for commercial Platinotype; thus, William Willis was spurred on to seek more economical alternative products.

2.1 Sources of platinum

By 1906, 98% of the World production of platinum was coming from Russia.²⁸⁹ The small remainder was supplied mainly from Chocó in Colombia, the site of the metal's original "discovery". Russian platinum had been found in the eastern slopes of the Urals in 1819; extraction began in 1824, near Ekaterinburg (now Sverdlovsk) and production was declared a state monopoly in 1825. At the outbreak of World War I in 1914, the Russian Ministry of Trade and Industry prohibited the export of platinum, consequently the supply to the West dwindled, and shipments ceased entirely by 1917, the year of the Russian Revolution, when the interim Kerensky Government nationalised all mineral resources. For the ensuing seven years the rest of the world managed only on supplies from Colombia and Canada. Then in 1924 Soviet Russia resumed export of platinum to the West, but this trade dependency was soon diminished by the discovery in that year of the Merensky Reef in South Africa, which established the Rustenburg Mines, destined to become the major supplier of the West in future years via the precious metal refiners, Messrs. Johnson Matthey.²⁹⁰

2.2 Platinum catalysis

Platinum metal – especially when finely divided as 'sponge' or powdered 'platinum black' – proved to be the prime exhibitor of the important chemical phenomenon of catalysis,²⁹¹ a discovery attributed to Humphry Davy in 1817,²⁹² which was studied during the 1820s by Johann Wolfgang Döbereiner, who used it in 1823 to invent a platinum-activated table-lighter burning hydrogen gas – his formidable *Platinfeuerzeug*.²⁹³ Catalysis was only so-named finally in 1836 by Jöns Jacob Berzelius.²⁹⁴ In 1902, the foremost German physical chemist, Friedrich Wilhelm Ostwald (1853–1932), discovered the ability of platinum to catalyse the oxidation of ammonia to nitric acid.²⁹⁵ This discovery soon lost its innocence, and was ultimately to undermine the commercial viability of the Platinotype, because nitric acid, previously manufactured from imported saltpetre (potassium nitrate) or Chile saltpetre (sodium nitrate), is essential to the manufacture of explosives such as picric acid (trinitrophenol), nitroglycerine, and TNT (trinitrotoluene), and of the fertilizer, or explosive, ammonium nitrate. The strategic importance of these substances placed a premium on the precious metal catalyst itself.

Ironically, it was Ostwald who also devised in 1903 a reprographic process called "catatype" employing catalysis brought about by a platinum print used as

a template. A fully processed platinotype was closely contacted with a paper surface impregnated with an unstable chemical combination (for instance, of potassium bromate and pyrogallol – one a strong oxidant, the other a reductant, respectively), and the platinum black catalysed their chemical reaction to produce a red coloration, providing an image which could be repeated. Other oxidation–reduction reactions were also employed catalytically, particularly involving hydrogen peroxide, to enable the offset printing of multiple images from a platinotype.²⁹⁶ Other manifestations of the catalytic power of platinum black are the phenomenon of image offsetting or "autoplating" (§9.8), and its use in the electroless deposition of non-noble metals (§4.8).

2.3 Price history of platinum

Economic considerations are a key factor in the history of platinotype and palladiotype artistic practice. Following the discovery of platinum catalysis, its price began an exponential rise as shown in Fig. 2.1.²⁹⁷

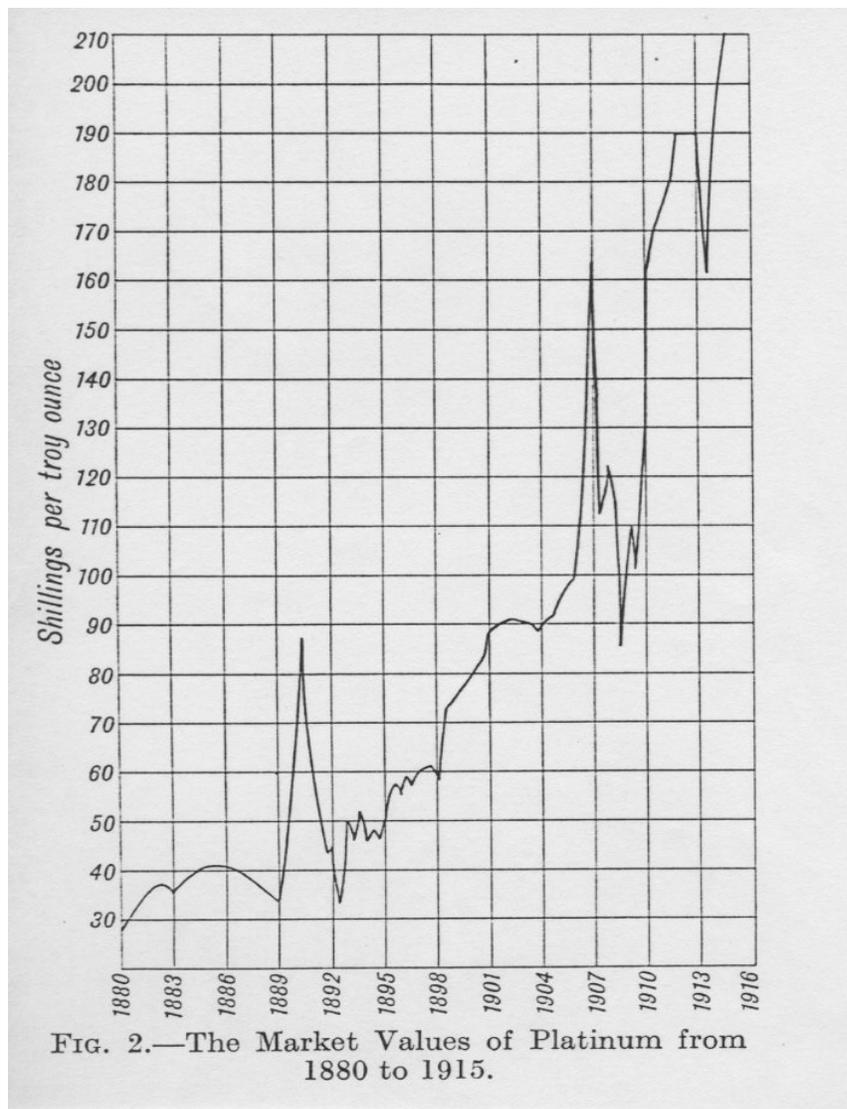


Fig. 2.1 The price of platinum 1880–1916

The use of platinum for filaments in incandescent light bulbs also caused a bill to be passed in Germany as early as 1901, banning its use in that country for photography.²⁹⁸ The price soared to an early peak in 1920 at £40 Sterling (800 shillings) per troy ounce (31.1 grams), but in the Great Depression it dropped to a minimum of 93 shillings per ounce in 1931. Platinum catalysts were used in the manufacture of sulphuric and nitric acids, which are vital feedstocks for the chemical industry, and both essential for explosives manufacture. Thus, platinum – a metal previously only of scientific interest for constructing chemically-resistant apparatus – was swiftly elevated in the first decade of the 20th century to the status of a highly protected, expensive, and very scarce strategic material.²⁹⁹

2.4 Alternatives to Platinotype: Nicol's kallitype

The platinum aesthetic soon came to exercise a considerable hold on the sensibilities of many photographic print-makers. But in view of the inflating cost of platinum, several of the more experimentally-minded were induced to seek a less expensive siderotype process that employed silver as the image substance, while still displaying the same characteristic look as platinum, with a matte surface and neutral or sepia colour, as described in §1.9. The iron-based silver process known as kallitype, and its subspecies called brownprint, sepiaprint and van Dyke, or van Dyck, are all variations – and sometimes needlessly complex elaborations – on Herschel's original argentotype of 1842 (§1.3). The most notable of these alternatives was invented in 1889 by Dr. William Walker James Nicol, an academic chemist at Mason College, Birmingham, and it was named by him as kallitype (Greek: καλλι = beautiful).³⁰⁰ Nicol made his motives clear in a retrospective letter to the *BJP* in 1891:

“For years I had believed that it ought to be possible to discover a silver printing process, which in point of simplicity and artistic effect would rival the expensive platinotype, and be able to claim for its results a degree of permanence higher than that possessed by ordinary silver prints.”³⁰¹

But as Nicol's letter goes on to recount, the initial attempt at marketing such a paper, by the newly-formed Birmingham Photographic Company, failed commercially because a choice of faulty paper stock caused rapid image fading. Once this was rectified, the process gained some acceptance among amateurs, many of whom chose to coat the paper themselves with sensitizer, evolving endless minor variations on the principal theme. The complex history of the kallitype process has been investigated in depth by Dick Stevens, and is described in his scholarly and painstakingly researched book of 2013, *Kallitype: the Process and the History*.³⁰² It soon became apparent that kallitype could claim to share all the characteristics of platinotype except the two most important ones: simplicity of operation and permanence.

Despite its popularity among amateurs, which is evident from numerous articles in the photographic journals of the early 1900s, this iron-silver process appears to have generated remarkably few surviving historical print specimens that have been identified as such. Dick Stevens, in his assiduous survey of many major photograph collections in the USA, found in total only *one* historic

kallitype; consequently he infers that the better-known – and therefore collectable – photographic artists did not make use of the process, but preferred platinum. Likewise, in response to a wide-ranging internet enquiry by the present writer some years ago,³⁰³ only a handful of kallitypes were reported by curators and conservators to have been positively identified in their collections dating from 50 to 100 years ago, when the process was enjoying its heyday. Differing explanations have been put forward to account for this extreme rarity. It is possible that specimens were rejected as uncollectable, like cyanotypes in Britain, because the process was deemed to be in some respect inferior. This is implausible if the process was sound, because kallitypes did not suffer, like the cyanotype, from a colour that was aesthetically unacceptable in some eyes, and other types of brown or black plain-paper silver print were keenly collected. Alternatively, specimens may have been collected, but they may have deteriorated and been disposed of or de-accessioned; this seems unlikely in view of curatorial scruples and the thoroughness of museum record-keeping.

In contradiction, it has been argued by certain promoters of the process that there are actually multitudes of historic kallitypes “out there” in collections – but they have not been identified as such because they are masquerading as bogus platinotypes.³⁰⁴ As yet, no substantive evidence has been offered to support this speculation. The myth appears to originate from letters to the periodical, *Photographic News* ca. 1901–6, in which the writers complained that a few unscrupulous commercial photographers were cheating their customers by supplying prints described as platinum which were actually on a matte silver bromide paper (not, it should be noted, kallitypes).³⁰⁵ To suggest that such fraudulent misrepresentation of platinotype was a widespread practice is a canard that unjustifiably demeans the ethics of the commercial photographers of the day.

The dearth of surviving historical specimens of kallitype is the strongest indication we have that this process, as practised at the time, was unreliable, and that many of the prints it yielded may have been short-lived; it certainly acquired this reputation among some influential photography writers of the day. Paul Anderson, for example, in his 1913 review of photographic printing media, see §2.11, is frank in his condemnation, stating that:

“...the [kallitype] image is so unstable that the process should be used for only the most ephemeral work. This statement will doubtless provoke violent protest from enthusiastic Kallitype workers, but it is true nevertheless ... this medium is not advised for work of any importance.”³⁰⁶

Anderson goes on to quote (somewhat inaccurately) from “a well-known worker” to this effect; his unattributed quotation actually comes from Roger Child Bayley, also writing early in the 20th century with typically sardonic wit:

“Kallitype is another printing process – or rather was, for nothing is heard of it now – and a batch of kallitype prints turned out of a drawer the other day bore no sign to distinguish the front of the paper from the back. The image which once had been vigorous enough, had folded its tents like the Arab and had silently stolen away.”³⁰⁷

Dick Stevens, however, has expressed the suspicion that Child Bayley's experience with kallitype may have been limited and his practice somewhat uncontrolled, and Stevens further points out that Anderson reported no laboratory tests on the permanence of kallitype, so his condemnatory conclusion does require further substantiation.³⁰⁸

While there is no doubt that freshly-made kallitypes can display vigorous 'platinum-like' images, the very few 100-year-old specimens that have now been identified in collections do show pronounced image fading and seriously yellowed highlights, suggesting the presence of residual iron(III).³⁰⁹ In early 20th century amateur archives, the present writer has also identified a few probable specimens of kallitype that are mostly very deteriorated, showing severe iron stains, fogging, and fading. Current practitioners of kallitype wisely hedge their bets by toning their prints with platinum, palladium, or gold; indeed, most workers today insist that this is essential to their permanence. A notable practitioner, Sandy King, claims that the process of toning kallitypes does not just coat or encapsulate the silver particles with the more noble metal, but totally replaces them with it.³¹⁰

2.5 Willis's "Satista" and "Satoid" papers

Resembling the kallitype, as an economic solution to the soaring price of platinum, Willis introduced and patented in 1913 a compromise product which was reminiscent of his very first platinotype papers of 1873–8: he used as image metal a mixture of platinum and silver, but predominantly the latter, making it substantially less expensive than Platinotype.³¹¹ The name he chose for this product, "Satista", derives from the Latin for "good enough" or "it satisfies".³¹² Unfortunately, in the long term, it did not. Although descriptive articles claimed that:

"the paper would give very fine black prints closely resembling Platinotype."³¹³

this process proved to be an uneasy hybrid: part kallitype, part platinotype, part salted paper print; details of the chemistry of this flawed process are discussed in §5.8. Willis maintained that Satista prints were permanent on the rather self-contradictory grounds that, even if all the silver in the image faded, the remaining platinum could still be sufficient (the amount was variable, according to the patent) to retain all of the original image detail. It appears that Satista papers were made in two varieties: one to give a black image only by room temperature development, the other to furnish a brown image when developed hot (40–70°C). Both types were coated on a hard-surfaced semi-matte paper base similar to the parchmented paper used for Japine Platinotype, and tests were reported of its resistance to fading with impressive results.³¹⁴

Later, in 1916, the Platinotype Company introduced a similar platinum metal-silver paper named "Satistoid", which was said to yield "deep rich brown tones" by room temperature ("cold bath") development in proprietary "Satistoid" developing salts, which were also used at greater dilution for the clearing process, followed by a hypo bath. *The Photographic Dealer* at the time eulogised this in the following terms:

"A Marvellous Production.
Platinotype Superseded.
Something for the Dealers this time." ³¹⁵

But it did not seem to fulfill its promise. It is not yet known if "Satistoid" paper was indeed platinum–silver, or whether it might have been a palladium–silver paper; analysis may reveal this.³¹⁶ The name of this paper appears to have soon become contracted to "Satoid",³¹⁷ possibly to avoid confusion with "Satista".³¹⁸

The 'window of opportunity' to use Willis's Satista and Satoid papers was fortunately rather small – they were launched in 1913 and 1916 respectively, and ceased to be advertised by 1929 – so relatively few artists made use of them. However, the wartime shortage of Platinotype paper did induce some printers to turn to these alternatives including the celebrated American photographer Paul Strand (1890–1976), see §3.10. A few of his most important works were printed in this medium *ca.* 1916, and have since suffered significant image deterioration, including fading and discoloration of the mid–tones, which has attracted the attention of photograph conservator, Lisa Barro (see §5.8).³¹⁹

Surprisingly, in 1925, Frederick H. Evans (1853–1943) made and published "representations" of a set of woodcuts by Edward Calvert;³²⁰ these Evans' facsimiles were catalogued as Platinotypes, because he had previously made use of this medium in 1913 and 1917 to print and publish enlarged Platinotype reproductions of sets of wood engravings by Hans Holbein and drawings by Aubrey Beardsley (see §1.13).³²¹ However, the observation of some fading in the Calvert reproductions aroused later doubts about the correctness of this process attribution, and subsequent instrumental analysis at the V&A in 1992 by Dr. Jacqui Rees showed that these prints definitely contained silver, as well as platinum, and probably were made on Willis's Satista paper (see §5.8).³²²

2.6 *Platinotype embargoed in Britain*

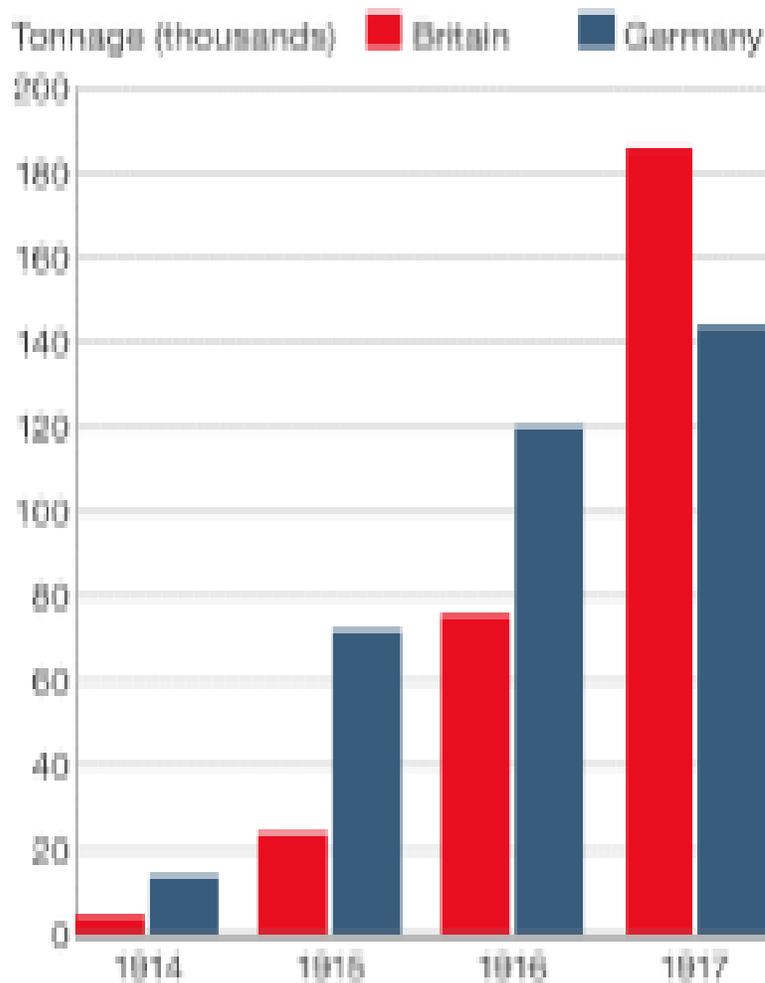
By 1916, the metal platinum had acquired strategic status as an essential catalyst to enable the manufacture of the vast quantity of nitrate explosives needed to prosecute the First World War (fig. 2.2).³²³ Finding this a more compelling employment for platinum, the British Government consequently imposed an embargo on its use for any purpose other than munitions manufacture (fig. 2.3)³²⁴ – an embargo which was later exacerbated by the 'platinum famine' resulting from the Russian Revolution of 1917 (§2.1). The British legislation effectively put a stop to Willis's manufacture and export of his Platinotype papers to the USA until after the end of the War. In the May 1916 issue of *The Photo–Miniature*, the editor, John Tennant, bemoaned the prospects for photography:

"The present scarcity of platinum and the consequent difficulty of obtaining supplies threaten to take all platinum papers off the market. This is an incalculable loss to pictorial photographers, since it must be conceded that no printing medium thus far introduced can approach platinum paper in pictorial possibilities." ³²⁵

Meanwhile throughout the war years, issues of the authoritative annual *The British Journal Photographic Almanac* entirely omitted any mention of the Platinotype process from its editorial *Epitome of Progress*, with no remarks even about its unavailability.³²⁶ In 1917, 1918 and 1919 the *Progress* section headed *Platinum Printing* carried only descriptions of Willis's Palladiotype paper; there were no comments whatever on the dearth of platinum. The subject was evidently a sensitive one at the time.

Winning the war in the factories

British and German World War I explosive production



Source: Niall Ferguson, *The Pity of War*

Fig. 2.2 Production of Explosives for World War I

**PLATINUM FOR
MUNITIONS.**

**DEALERS TO FURNISH DETAILS
OF STOCK.**

The following circular, signed by Mr. L. W. Llewelyn, Director of Materials at the Ministry of Munitions, has been addressed to dealers in platinum:—

I am directed by the Minister of Munitions to inform you that, in exercise of the powers conferred on him by the Articles of Commerce (Returns, &c.), Act, 1914, pursuant to arrangements made with the Board of Trade, he hereby requires you within three days from the date of this notice to make a return to the Director of Materials of the Ministry of Munitions, Armament-buildings, Whitehall-place, S.W., of the whole of the stock of platinum, ores, residues, or bars containing the same, now on your premises or under your control.

I am at the same time to draw your attention to Defence of the Realm Regulation 30A, and to the Order made by the Minister of Munitions thereunder, and I am to observe that any person buying, selling, or dealing in platinum, or goods manufactured wholly or partly of platinum, offering or inviting an offer or proposing to buy, sell, or deal in it or them, or entering into negotiations for the sale or purchase of or other dealing in it or them, without a permit, is liable to the penalties provided for offences against the Defence of the Realm Regulations.

**RESTRICTED SALE OF OPTICAL
INSTRUMENTS.**

It is notified in the January Army Orders that dealers in optical munitions, such as binoculars, telescopes, prismatic periscopes, prismatic compasses, &c., have been placed under restriction with regard to the sale of these instruments under the Defence of the Realm Act Regulations, 1914, and may only offer for sale those specially marked.

Two marks will be used, one indicating instruments which do not come up to the standard Government requirements, and the other instruments which come up to the required standard, but are not required by the Government.

PAY OF OFFICER PRISONERS OF WAR.

Mr. Forster, in a Parliamentary answer, gives the following details of the pay and allowances of British officer prisoners of war:—

The general rule is that regimental officers are credited with full pay and lodging, fuel and light, and field allowances. Staff officers receive staff pay and field allowance for 61 days, after which they receive regimental pay and allowances, if regimental officers, or half-pay and regimental allowances if not regimental officers. The issues made to the officer himself by enemy Governments are:—

Germany and Austria.—To captains and above, £5 a month; subalterns, £3 a month.

Turkey.—To captains and above, 4s. 6d. per day; subalterns, 4s. per day.

These sums are deducted from the amounts credited to the officer's personal account from Army funds.

PLATINUM FOR MUNITIONS.

Mr. Lloyd George, in a written answer to Colonel Gibbs, states that the recent regulations in regard to platinum are meant to include the platinum which had already been used for mounting ornaments of jewelry.

Arrangements are being made with the representatives of the trade by which permission will be given to sell their existing stocks of jewelry, provided that a guarantee is given that, until further notice, no platinum will be used for mounting or manufacturing jewelry.

THE EXPORT OF COCOA.

Messrs. Cadbury Brothers (Limited) write with reference to statements that cocoa exports to Holland, Denmark, and Scandinavia have been in 1915 34,520,987lb., that they believe the bulk of these exports is raw cocoa, the export of which they never touch. Their exports of prepared cocoa in 1915 were 56,030lb. in fulfilment of contracts made in 1914. They have consistently advocated the prohibition of exports of cocoa to the above countries during the war.

Fig. 2.3 Entries from The Times 7 & 12 January 1916

In 1918 the Platinotype Company resumed its advertising of Platinotype in the British photographic press – but in the poignant context of World War I, as can be seen in fig. 2.4.³²⁷ There is a touching irony hidden in this recommendation that family photographs of "sons and brothers" should be immortalized in the same precious metal that could have been instrumental in their destruction as fighting men.

PLATINOTYPE AND PALLADIOTYPE

The British Journal of Photography, February 15th, 1918.

"A Black Platinotype print possesses an image which is so unalterable that it rivals its paper support in permanence, and justifies the remark of Mr. Chapman Jones (in 'Photography of To-day,' p.196) that, 'There seems every reason to suppose that if Platinum prints had been made in Abraham's time, or when Egypt was at the height of its glory, they might, if preserved with reasonable care, have been available for our information at the present day.'

"Palladiotype prints, recently come into use, as the result of the restriction on Platinum, presumably are just as permanent as those by the ordinary Platinum process. This is only an inference from the known properties of Palladium metal, but it is no doubt one which experience, as time goes on, of Palladiotype prints will confirm."

AVOID PAPER WHICH WILL QUICKLY FADE, AND INSIST UPON HAVING THE PHOTOGRAPHS OF YOUR SONS AND BROTHERS PRINTED IN EITHER PLATINOTYPE OR PALLADIOTYPE.

THE PLATINOTYPE CO. - - 66, Beckenham Road, PENGE, S.E.20.

Fig. 2.4 Advertisement by the Platinotype Company, 1918

By 1920, supplies of Platinotype paper had come back on stream,³²⁸ but at such excessive prices that there was serious doubt if this medium of photography could be sustained:

"The question arises whether the process of platinum printing is not in danger of extinction."³²⁹

In the USA *The National Woman's League for the Conservation of Platinum* was founded by Mrs Ellwood B. Spear in 1918,³³⁰ with the backing of the American Chemical Society.³³¹ Patriotic American photographers were confronted with an ethical as well as a financial dilemma when selecting their print medium,³³² and serious consideration was being given in the American photographic press to the alternatives to platinum, such as palladium and kallitype, see §2.4.³³³

By the time that Western civilization had relinquished the first of its near-successful attempts at self-destruction, the price of platinum had risen to five times that in 1900. To counter the soaring costs, Willis again responded to the challenge with an innovation, as he had in 1913 with his Satista paper, in which silver replaced most of the platinum (§2.5): in 1917 he devised his Palladiotype paper, using the closely related noble metal palladium, which had not yet found strategic applications. These developments probably helped extend the lease of life of the Platinotype Company, which was not finally wound up until 1937.

2.7 *Palladium supplements platinum*

The element palladium was discovered in platinum ores by William Hyde Wollaston (1766–1828) in 1803; by 1916, it had long been recognised as another potential means of siderotype photography.³ Tentative processes for palladium printing had previously been suggested: first by Burnett (1856),³³⁴ then by Willis himself (1878),³³⁵ and Pizzighelli and Hübl (1882),³³⁶ but palladium was not used as a substitute for platinum printing in the early days because it was even more scarce than platinum at the time, and the image was found to be more prone to "solarization" when heavily exposed (see §3.7). However by the 1890s, the use of palladium as a means of toning silver images was well-established in order to make photoceramic prints, which thereby gained resistance to kiln-firing under a glaze.³³⁷ Palladium toning of silver prints was acknowledged in several manuals of the day,³³⁸ and deemed to give similar results to platinum, but dismissed as impractical because palladium was much more costly than platinum at the time – 6 pence per grain or £12 per ounce, compared with ca. £2 per ounce for platinum.

Baron Arthur von Hübl in his comprehensive German handbook of 1895, *Der Platindruck* (§1.16), recommended the employment of a mixture of palladium and platinum in the sensitizer in order to impart sepia print tones. The relevant passage, translated below, also emphasises the importance of humidity in determining the outcome with palladium-containing papers:

"Platinum papers for brown prints can be prepared both by the addition of palladium as well as mercury salts, but the palladium additive is particularly suitable for the self-development process just discussed. Palladium-platinum papers only give brown images if they are printed when completely dry; if damp, the paper always provides black prints. Such dry paper has to be exposed with the help of a photometer, because the resulting image is barely visible in iron oxalate double salts. The palladium-containing platinum paper delivers beautiful, pure brown-coloured and well-modulated images, surpassing in this respect the hot development of mercury-containing paper. Unfortunately, this is a very difficult treatment because of the previously mentioned sensitivity to moisture."³³⁹

In a series of English digests of the second edition of von Hübl's monograph on platinum printing,³⁴⁰ published in 1902, E.J. Wall repeated the recommendation of an admixture of about 20% palladium to the platinum.³⁴¹ Twenty years later, Wall repeated and elaborated this advocacy of mixed platinum-palladium sensitizers in the third of his series of articles on "The Iron Salts" in *American Photography*.³⁴² It is surprising that William Willis seems never to have adopted mixing a small amount of palladium with his platinum to

³ *Etymological footnote 3: The word siderotype was first coined in 1842 by Sir John Herschel from the Greek for iron, sideros = σιδηρος. It is a useful collective noun for all the iron-based photographic printing processes: platinotype, palladiotype, cyanotype, kelainotype, kallitype, van Dyke, chrysotype, argentotype, argyrototype, etc. See §1.3.*

overcome some of the difficulties that arise with using the latter alone; however, there is new evidence uncovered by the research of Alisha Chipman into Paul Strand's work (see §3.10) that the Platinotype Company may have made small additions of palladium to their special Platinotype paper, during the last years of its production, 1932–37. The mixing of the two noble metals for image-making was not due to become common practice until the 1970s, when it was taken up by Irving Penn and others, as will be seen in §4. But the exigencies of wartime in 1916 were soon to enforce the adoption of palladium entirely by itself, as a total substitute for platinum printing.

2.8 Palladiotype launched by Willis

The obligatory switch of noble metal for photography from platinum to palladium took place quite abruptly in 1917 when, in response to the British Government's embargo on platinum photography, Willis devised and launched his Palladiotype paper. The first hint of this innovation came with an unexpected demonstration in January 1917 by Mr. William H. Smith, the Technical Manager of the Platinotype Company, to a meeting of enthusiasts at the local Croydon Camera Club,³⁴³ of which he was a prominent member. Without disclosing that it was actually palladium, he simply introduced the product as a "brand new printing paper" and a "radically new departure".³⁴⁴ It met with the general approval of the Club members. On 8 March, the same luminary demonstrated the newly-revealed "Palladiotype" to the more august Camera Club of London, together with the Platinotype and Satista processes.³⁴⁵ He showed that both developing and clearing of Palladiotype were accomplished simply with baths of 5% potassium citrate solution acidified with 0.26% citric acid. The tendency of Palladiotype to "solarise" (see §3.7) was acknowledged, and contrast enhancement by dichromate was also described. In the vote of thanks to the speaker it was prophetically remarked:

"The introduction of this new printing process would be one of the landmarks of the history of photography."

Willis & Clements in the USA first advertised the paper in 1917 as "Palladiotype Sepia",³⁴⁶ but by 29th June the commercial product was being described in England as "Sepia Japine Palladiotype paper",³⁴⁷ which may also have been referred to in more familiar terms as "Sepia Vellum" in the USA. Willis & Clements also stamped the paper sheets on the *verso* with "W & C Palladio",³⁴⁸ which may explain Stieglitz's use of the term in his letters, see §3.5.

Following the Japine surface sepia paper, matt surface varieties of Palladiotype paper were advertised by Willis's Platinotype Company in March 1918 and publicly demonstrated once again by W.H. Smith.³⁴⁹ The newly marketed papers were designated as Matt Rough and Matt Smooth on white stock, and Matt Smooth on buff stock, and all described as "Warm Black Palladiotype" papers.³⁵⁰ In 1921, Ernest Albert Salt, Departmental Manager of the Platinotype Company claimed that the Company's Palladiotype papers had just undergone a very significant improvement,³⁵¹ and in 1922 the Company proudly announced a "further reduction" in the prices of its Platinotype and

Palladiotype papers.³⁵² The Company continued to produce Palladiotype paper until its closure.³⁵³

2.9 Processing of Platinotype and Palladiotype

The chemicals for processing these two kinds of paper, as recommended by William Willis, were quite different. Platinotypes were customarily developed in dipotassium oxalate solution, slightly acidified, the recommended strength was ca. 25% w/v, but some workers preferred a solution nearly saturated at 33% w/v. Before 1892 the developer solution was used hot (140–170 °F, 60–77 °C) to accelerate the chemistry of platinum precipitation and provide an adequate image quality; the elevated temperature was also said to promote a "very slight warmth of tone" in the blacks.³⁵⁴ After 1892, the preference shifted to Willis's new "cold development" papers, which were welcomed for their easier use at room temperature.

As a modification, said to generate cooler, bluish tones, the Company also marketed its proprietary "Special D Salts" Platinotype developer, which we now know contained the following substances in the approximate proportions (% w/w) indicated:³⁵⁵

Potassium oxalate monohydrate	85 %
Potassium dihydrogen phosphate	12 %
Oxalic acid dihydrate	3 %

The mixed salts were dissolved in sufficient water to make the working strength of only 8.6% w/v for the developer for black papers at room temperature, and of 10.3% w/v for the Sepia Japine papers at 70–80 °C, although some workers used more concentrated developer.

Black Platinotypes were then directly cleared for about 10 minutes in each of three successive baths of hydrochloric acid, in which the concentrated acid (36% w/w) was diluted 1:60 (0.2 M, pH<1); but for Sepia Platinotypes a more dilute acid of half that strength was recommended. These clearing procedures were intended to remove the residual iron salts from the print, but were not always successful (see §9.1) and some workers employed much longer clearing times. Finally the print was washed in water for about 20 to 30 minutes.³⁵⁶

For his Palladiotype papers, Willis recommended that they be developed in trisodium citrate (20% w/v) acidified with added citric acid (2% w/v); cleared in the same, 8x diluted (2.5% w/v), but with added citric acid (1.2% w/v), three baths of 10, 15, 20 minutes, followed by a water wash.³⁵⁷

William Willis was a shrewd and observant chemist, painstaking in his perfection of process.³⁵⁸ He would not have recommended his new citrate developer and clearing agent for Palladiotype if he thought his existing Platinotype developer of potassium oxalate would serve satisfactorily. What drove Willis to recommend the different procedure for Palladiotype? There is an indication in the *Abel's Weekly* article:

"The Palladiotype developer and clearing baths have no tendency to injure the beautiful surface of the paper employed for coating. An undue immersion of matt Platinotypes in the oxalate and acid baths does tend to destroy their natural bloom." ³⁵⁹

The consequences of using both oxalate and citrate developers for Palladiotypes have been tested and compared in the present work (fig 6.7, §6.18). It has been found in general that the oxalate developer solution tends to give slightly higher densities and warmer image colour in palladium prints, but it does cause a perceptible chemical fog in the high values, which is worsened by humid conditions.³⁶⁰ It should be noted that Willis did not advise clearing Palladiotypes in hydrochloric acid like Platinotypes, but recommended the milder acidified citrate solutions. If hydrochloric acid is used to clear Palladiotypes one can expect some loss of image densities compared with citrate clearing. However, if the Palladiotype has also been developed in oxalate it will be somewhat fogged, which can be partially 'cleared' by the hydrochloric acid – a case of two errors in processing being somewhat self-compensating! The chemical fog caused by developing palladiotypes in oxalate will also be mitigated if a contrast-enhancing agent such as chlorate or hexachloroplatinate(IV) is used in the sensitizer or dichromate in the developer bath, as is recommended in some contemporary practice – see §6.5.

The converse procedure, of using a Palladiotype citrate developer to process a Platinotype seems not to have been tested in modern times, since Tina Modotti suggested it to Manuel Alvarez Bravo, ca. 1928 – see §3.2.

2.10 Later history of the Platinotype Company

William Willis died in 1923, a bachelor, at the age of 82. Obituaries in the photographic press remembered him chiefly for his invention of the Platinotype process, but also acknowledged his polymathic interests, as an accomplished musician, conversationalist, and as a scientist who contributed to spectroscopic analysis.³⁶¹ Control of the Company then passed to his younger brother, John Willis (1843–1930) as sole proprietor, who promptly incorporated it as a private limited company, registered on 14th January 1924 with a nominal share capital of £12,000. Charles Robinson was appointed as managing director and, as director and secretary, Alfred Willis Clemes (1887–1971), a mining engineer and Rhodes Scholar (Oxford, 1908), who was a first cousin once removed of William Willis, from the branch of the family that had emigrated to Tasmania, ca. 1886.³⁶² However, this commercial status as The Platinotype Company Limited was relatively short-lived: in July 1928 all of John Willis's remaining shares were transferred to the two directors, and the limited company was finally wound up on 30th August 1932 at a general meeting held by Charles Robinson, the current chairman.³⁶³

Ownership having been transferred to the directors, Robinson and Clemes in partnership, on 30th November 1931, the once more delimited Platinotype Company remained in business, as the only manufacturer of platinum papers in the world, until the summer of 1937, when the coating plant was shut on the 20th June, and the Company was finally dissolved. At this time the papers offered by the Company were as summarised in Table 2.1.

A notable late user of Platinotype Company products in England was Dr. J.R.H. Weaver, the President of Trinity College, Oxford, whose unopened tins of Platinotype and Palladiotype paper dated 1936 and 1937, were donated by his son to the Museum of the History of Science in Oxford, on his father's death in

1965 (Table 2.1).³⁶⁴ Weaver was a distinguished photographer during 1910–1930 of church architecture, especially in Spain, and was exhibited in 1945.³⁶⁵ He was a friend of Frederick Evans, whose portrait he printed in sepia Platinotype, and whose obituary he wrote for the *Photographic Journal*.³⁶⁶ Weaver bequeathed a large archive of his printed work to the V&A Museum, including 150 Platinotypes and Palladiotypes.³⁶⁷

The last of the Company's stock of Warm Black Japine Platinotype paper, "W.B.J." specially coated at the behest of Paul Strand, (see §3.10), was sold in July 1937 to Hollywood photographer Ned Scott (1907–1964), whose archive, curated by his son Norman, has proved to be a valuable source of information, in the absence of any surviving records of the Platinotype Company in Britain.³⁶⁸ Both Ned Scott and Paul Strand then tried to obtain information from the Platinotype Company about coating their own paper. Charles Robinson replied in a letter to Ned Scott in 1937 with a telling observation that now stands as a fitting epitaph for the commitment of William Willis and his Company:

"There is so much to be covered; the paper surface alone took us years to master, and the chemistry a lifetime." ³⁶⁹

While the information was promised, we have no record that it was ever sent, and there are no surviving Company records.

It is uncertain when the Willis & Clements Company wound up its business in Philadelphia; they are still mentioned in the *Photographic Journal of America* for June 1916 as supplying 'Japine Silver' paper,³⁷⁰ but in the following volumes of 1917–18 they do not feature at all. There are however advertisements by Willis & Clements as late as 1928 in *Photo-era Magazine*, mainly for camera equipment.³⁷¹ In 1931 Willis & Clements' agency for the Platinotype Company was terminated, and their papers were thereafter supplied directly from the Company in London to clients in the USA, such as the photographer Ira Martin at the Frick Art Reference Library (see §3.10).³⁷²

The ultimate demise of the Platinotype Company can be attributed to the limitation that constrained all the siderotype processes: the near-necessity for printing by contact, using a same-sized negative, to allow a sufficient throughput of light. Enlarging onto platinotype paper by projection called for very lengthy exposures and specialised light sources and optical systems (§1.11), not commonly possessed by the amateur. The growth in popular use of miniature cameras in the 1930s, recording negatives on rollfilm, required easy enlargement; but convenient exposure times for printing by projection demanded a sensitivity that only developed-silver halide photography could offer, thus guaranteeing its commercial dominance for most of the 20th century.

2.11 *Rôle of Paul Anderson in the USA*

Platinum printing became an important photographic medium in the USA, in large measure because it was taught at the renowned Clarence H. White School of Photography, which was founded in 1914 and closed in 1932, and could claim to be the only school in the USA dedicated to 'art photography'.³⁷³ Several famous alumni of the White School became noted exponents of platinotype, as will be described in §3.12. They owed their acquired skills to the fact that, in

the early years of 1914–18, Clarence White had hired Paul Lewis Anderson (1880–1956), an electrical engineer, as an instructor on the faculty to teach the techniques of photography. Anderson had already become a great advocate of platinum printing with his publications of 1913, in which he stated that platinum met all seven of his criteria for selecting a printing paper: permanence, repeatable printing, easy control and manipulation, modifiable image color and paper texture, and foremost, quality.³⁷⁴ His handbook of 1917 was based on his White School lectures, an appendix to which shows that he had already made a start then on experimenting with palladium:

"Since Chapter X was written, commercial platinum paper has practically disappeared from the market, owing to the use of this metal for military purposes, and its place has been taken by a paper in which the salts of palladium are employed, palladium being one of the rare platinum group of elements. There seems no reason to doubt that palladium paper will give prints fully as permanent as those made with platinum, and though the writer has not had opportunity to experiment extensively with the new product, it seems quite on a par with the older paper as regards quality and convenience."³⁷⁵

When the closure of the Platinotype Company in 1937 suddenly deprived fine-art photographers in the USA of their favorite print material, some were quick to rediscover the methods for preparing the sensitizer and hand-coating their own platinum papers. Anderson was in the forefront of republishing formulae in 1937–8,³⁷⁶ and the opening remarks of his 1938 article are very significant to the present study:

"However, palladium paper never became very popular, at least in this country [the USA], I believe, because the technique of processing advised by the makers was different from that used in the case of platinum, and partly because it was difficult to convince the users of the older paper that anything could rival their beloved platinum..."³⁷⁷

Anderson's instructions for palladium printing continued to ignore the processing procedure recommended by Willis & Clements, and instead specified the same developer as was used for platinum (near-saturated potassium oxalate solution) but with clearing in weaker hydrochloric acid, 1:200 diluted, because he found that the 1:60 strength used for platinum, dissolved a significant amount of the palladium image (for chemical reasons, see §11.4). It is a conjecture that Anderson's published method may have reflected Stieglitz's earlier Palladiotype practice of 1917–27, of which we have no record, but which it is important for us to infer. Connections between the two men have been sought: it appears that they had a mutual acquaintance during the years 1914–17 in Karl Struss (1886–1981), who shared a photographic studio with Anderson in New York opposite Stieglitz's *291 Gallery*, at which Struss exhibited his own work, which was also published by Stieglitz in his celebrated periodical, *Camerawork*.³⁷⁸

In his 1938 article, Anderson also acknowledged a Dr Karl Schumpelt for first demonstrating the method for hand-sensitizing and processing palladium paper "practically identical with that used for platinum", which Anderson himself

had published in 1937. Anderson evidently obtained his palladium salt supplies from Schumpelt's company, Baker & Co., the major precious metal importers and refiners of Newark, New Jersey. Surprisingly, we find that in 1941 Schumpelt was granted a US Patent for a palladium printing process,³⁷⁹ although his patent specification contained nothing new, that had not previously been published by Anderson.

The procedures for platinum printing recommended by Anderson were based on the method of contrast control by 'drop counting' the volume of an added oxidant, potassium chlorate in ferric oxalate solution, which originated with Pizzighelli and Hübl, §1.16. This subsequently became standard practice in the USA: witness the standard American reference works by Henny & Dudley (1939),³⁸⁰ Wall & Jordan (1940),³⁸¹ Arnold Gassan (1977),³⁸² and William Crawford (1979).³⁸³ These methods continue to be advocated in contemporary manuals, such as the comprehensive handbook by Christopher James (2013), which is widely used by practitioners today.³⁸⁴

3. Early 20th Century Platinotype and Palladiotype

The dominant figure in American photography throughout the first three decades of the 20th Century was Alfred Stieglitz (1864–1946), who did much to promote the Platinotype process, which had been rather neglected in North America despite the commercial endeavours of Alfred Clements. Stieglitz's important legacy of Platinotypes and Palladiotypes still stands as one of the cornerstones of photographic art,³⁸⁵ but is not entirely free from technical problems of conservation, as this chapter will reveal.

3.1 *Platinotypes by Alfred Stieglitz*

Stieglitz first made platinum prints in Germany during the period 1884–6, while he was studying at the Technical University of Berlin under the distinguished academic photochemist, Professor Hermann Wilhelm Vogel (1834–1898). Stieglitz coated his own platinum papers (see §3.5), and published frequently on the process in the German photographic literature,³⁸⁶ presumably well-informed by the extensive researches that had recently been published in German by Giuseppe Pizzighelli and Arthur von Hübl in 1882 (see §1.16),³⁸⁷ which he reported back in translation to the English-speaking readership elsewhere. While in Vienna, Stieglitz also tested the commercial papers being produced in Germany, finding, for the "direct printing" platinotype papers (§1.16), a variation of colour under a variety of humidity conditions during exposure and processing.³⁸⁸

In 1889 Stieglitz also had the idea of using a bath of his potassium chloroplatinite solution to platinum-tone silver photographs. On publishing this, he clashed in print with Lyonel Clark (see §1.5) in a dispute over which of them could claim priority for this invention: Stieglitz conceded by restricting his claim to a *simplified* platinum toning bath, admitting that Clark had publicly demonstrated a more elaborate method three months previously in 1888.³⁸⁹

Notwithstanding this early technical experience with platinum chemistry, it appears that, on returning home to the USA in 1890, Stieglitz never hand-coated his own papers thereafter, but always employed whatever commercial platinum papers were then available from suppliers (see §3.5). With his early publications in North America (1891–1902), Stieglitz became a powerful advocate for the neglected platinum medium, stressing the supposed advantages offered by the ease and speed of the processing:

"...and yet let me reassure you that many of my prize photos, all of which are still in as perfect condition as on the day they were made, were turned out inside of fifteen minutes, including printing, developing, fixing, washing and *mounting!*"³⁹⁰ [italics in original]

Compared with the conventional description of the process, a somewhat cavalier attitude might be thought to characterise this approach to wet-processing. With overweening confidence, Stieglitz even pared down his track record for a Platinotype to 10 minutes:

"When the development is completed, which usually takes from one to six minutes, the remaining iron salts in the paper are dissolved out in one or two minutes, by simply immersing the print in a weak solution of muriatic

acid and water... then a slight rinsing of the print for a minute or so in water is sufficient washing, when it may be dried and mounted... As to quickness it has no equal, for a finished mounted print which is permanent can be made from a negative inside of ten minutes." ³⁹¹

This accelerated *modus operandi* contrasts somewhat unfavourably with the measured pace traditionally recommended (see §6) for the duration of clearing and washing platinum prints, which amounted to at least an hour of 'wet time' – without even counting in all the other steps needed to produce a finished print. Stieglitz's lack of concern for ensuring permanence is the more surprising in view of his sardonic admonitions as an exhibition critic in 1892:

"I willingly grant that 99 per cent. of the negatives produced by the 'camera artists' ought to be printed on a most non-permanent process, for the sake of coming generations; but such pictures have no business at a large public exhibition – hence we need not consider them." ³⁹²

3.2 *The issue of "sloppiness"*

Stieglitz's self-proclaimed method for working Platinotype in 1892 presents a problem regarding any intended re-creation and simulation of his Palladiotype practice of 1917, which came 25 years later. After 1902, Stieglitz found no cause to disclose anything further about the technical aspects of his practice, thus leaving us uncertain whether his wet-processing procedure became more careful during the intervening years.³⁹³ If it did not, then the origin of problematic discoloration in his Palladiotypes (§3.8) is easily comprehended. In mitigation, it must be acknowledged that his last technical article in 1902 did bear the denunciatory title: "Sloppiness in the Platinum Process and its Effect", in which he condemned carelessness over the deleterious effects of moisture and light on platinum papers, and drew attention to the findings of Dr. Jacoby of Berlin concerning the inadequate clearing of platinum prints,³⁹⁴ which echoed those of Chapman Jones (§9.2) made many years earlier. His appeal sounds, at least in some degree, self-critical:

"Let us call a halt to our slipshod and sloppy technical manipulations and methods and revert to some measure of the old-time care and thoroughness." ³⁹⁵

After this final exhortation, we have very little more technical information to go on, except his chance remarks in letters to friends and suppliers of materials. Stieglitz's entire archive has been studied and reviewed by curator Sarah Greenough,³⁹⁶ and a useful summary of the processes and techniques he employed over the years 1914–1927 was presented by Julia Thompson to the CASVA Stieglitz Colloquy in 1993.³⁹⁷ Whether Stieglitz ever took his own advice in respect of curbing his "sloppiness" must still remain in doubt, because in a 1921 letter he confesses his contempt for orthodoxy:

"I do nothing according to instructions. If I follow them I might as well throw the cans of paper into our blazing fires." ³⁹⁸

3.3 Glycerine development of Platinotypes

The free-style approach to print-making adopted by Stieglitz in the interests of producing "artistic effects" is especially apparent around 1900 in his use of the so-named "glycerine process for the development of platinum prints", which he is credited with inventing then in collaboration with Joseph Keiley.³⁹⁹ However, Adrienne Lundgren has pointed out that Stieglitz, while discussing the processing of the newly marketed cold-bath platinum papers, first described the use of a glycerine developer as early as 1892 as a remedy for a poor-quality negative.⁴⁰⁰ William Willis also recommended the use of glycerine to the Camera Club in 1893 (§1.8).⁴⁰¹ Glycerine somewhat belies its naming as a "developer", however, because the presence of the viscous, inert, but water-miscible liquid glycerine actually *inhibits* and slows the development process, allowing time for a selective local application of developing agents by brush to achieve a differentiation of colour – often by means of mercury toning – and thereby conferring some painterly qualities on the production of the image, which acquired a greater sense of uniqueness. Lundgren has investigated how such local manipulation of the platinum image during development was also adopted by other noted practitioners such as Frederick Holland Day, Gertrude Käsebier, Clarence White, Paul Strand and Karl Struss.⁴⁰² However, Stieglitz himself did not continue with this *modus operandi* for long, for as his style progressed from pictorialism to modernism, so his technique reverted to 'straight' photography and unmanipulated printing. He was, however, still given to waxing his finished prints with beeswax to impart greater depth to the shadow tones.⁴⁰³

3.4 Multiple coating of platinum papers

Around 1913, a number of workers in platinum, in search of a longer tonal range and higher maximum density, adopted the technique of double-coating their papers with the platinum sensitizer. The procedure and a variety of formulae were first described in detail by Hermann Clemens Kosel (1867–1945), court photographer to the Kaiser, in a series of articles in the German photographic literature, which were translated, heavily edited and republished in *American Photography* by Walter Zimmerman as "Combination Platinum Printing".⁴⁰⁴

An even more laborious but flexible procedure, called 'multiple printing', was recommended by Karl Struss in the first issue of *The Platinum Print* in 1913:

"The theory of multiple platinum printing is quite simple, requiring but little practice to secure successful results: the idea being to superimpose image on image (by repeated sensitizings, printings and developings) until the required depth of tone has been obtained. Strange as it may seem, altho [sic] repeated printings add to the blacks, the print seems actually to lighten, due no doubt to the lengthening scale of tones or intermediate gradations, and the resulting increased contrast."⁴⁰⁵

Struss also suggested the extraordinarily expensive procedure of printing on the *verso*:

"It is a good plan to use enough sensitizer to soak thru to the other side of the paper, in order to print thereon simply by reversing the plate. Not only

does this double printing add to the quality of the blacks, but we get double the effect with but the one coating."

The celebrated American photographer Paul Strand (1890–1976) and his friend, the Hollywood photographer Ned Scott mentioned in §2.10, are known to have used "Warm Black Japine " papers which, at their request, had been enhanced by the Platinotype Company with an additional special coating whose details have not yet been discovered.⁴⁰⁶ No original source of Strand's experiments in double-coating platinum paper has been found, see §3.10. These methods of multiple coating and printing prefigure the practice later developed to great effect in the 1970s by Irving Penn (see §4.1).

3.5 Platinotype replaced by Palladiotype

Stieglitz enjoyed more than 25 years of successful platinum printing, with consummate skill, like many of his peers in fine art photography.⁴⁰⁷ From 1890 until *ca.* 1901, he had employed and publicly recommended the Platinotype Company's papers imported by Willis & Clements, but he transferred his allegiance when platinum papers began to be manufactured in the USA; notably to the range of American Platinum Papers launched in 1901 by the American Aristotype Company of Jamestown, NY.⁴⁰⁸ It appears from his correspondence with George Eastman that Stieglitz also made use of the Eastman Etching Black and Eastman Etching Sepia platinum papers marketed in 1909/10 by Eastman Kodak.

Then in 1916 the bombshell dropped: platinum became a 'prisoner of war'. In that year, Eastman Kodak in the USA ceased manufacture of their range of platinum papers, and Willis in England was obliged by law to stop producing and exporting his Platinotype paper to the USA, although a small supply of Sepia Platinotype paper was said to have got through, if we judge by the remarks of Clarence White in 1918/19:

"Black platinum paper practically disappeared from the market, but sepia platinum paper has been obtainable."⁴⁰⁹

If this was indeed the case, as Willis & Clements advertisements of the time suggest, it raises three questions: why did Stieglitz not make more use of Willis's Sepia Platinotype during the war years, but turn to the less satisfactory Palladiotype instead? Furthermore, how could Willis continue legitimately to market the one platinum-containing product, but not the other? Is it possible that Clarence White, who has been described as "an unskilled technician",⁴¹⁰ could mistake Palladiotype paper for sepia Platinotype paper?

Of particular curatorial concern to the National Gallery's investigation was Alfred Stieglitz's major use, during the decade 1917–1927, of the Palladiotype process, which is much less well documented, historically and technically, than Platinotype. Hence Palladiotype lay at the focus of the present study, at least in its initial stages.

From 1916 on, photographers everywhere were experiencing difficulty with the dwindling platinum supply and its soaring cost. That year, in a letter to the British photographer and author, R. Child Bayley, Stieglitz observed:

"So you can imagine what the cessation of the manufacture of that product means to me, especially now when I really have plenty of time to print... Of course I could make my own paper. I used to make it twenty eight years ago in Berlin for awhile, but making it properly, as I would want it, would mean much experimenting and I don't know whether I'd find time for both..."⁴¹¹

This admitted reluctance to perform all the experimentation needed to optimise hand-coating platinotype paper, reflects the extent to which the artist in Stieglitz's persona had, by this time, taken over from the scientist. We may therefore infer with reasonable confidence that he never prepared his own papers thereafter. It is evident from his letters to Paul Strand and others that the quality of the Palladiotype paper imported by Willis & Clements as a substitute for Platinotype rarely gave satisfaction at first; Strand, in his 1947 retrospective review of Stieglitz's life and work, summed up the shortcomings of Palladiotype but indicated how Stieglitz made creative use of its defective tendency to "solarize" – see §3.7 below:

"In this period platinum paper, which he had used for many years, became unobtainable and he turned to a sepia palladium paper as a substitute. This was a distinctly inferior material, unpleasantly warm in color but worst of all prone to quick solarization of the shadows. Ice in the developer helped to solve the problem of color. Then in the printing of certain negatives, never letting it become a trick or mannerism, he used the solarization deliberately to emphasise the linear elements, as for instance in the beautiful "Hands with Thimble." Here is an example of Stieglitz' creative use of materials and their importance to the making of his prints."⁴¹²

Stieglitz later referred to the paper as "Palladio",⁴¹³ and only by 1921–2 did he begin to express some satisfaction with the results:

"As for the Palladio black buff I tried it out some weeks ago. Finding it having enough quality in some ways made me write a letter to London. They are very close to producing a first class product."⁴¹⁴

This was at the time when Ernest Albert Salt, Departmental Manager of the Platinotype Company, was claiming that considerable improvements had recently been made to Palladiotype paper, and the medium was gaining acceptance by the leading photographers. But it would also turn out, to our enduring regret, that the Palladiotype process was intrinsically far less forgiving of Stieglitz's "sloppiness" in processing than the more robust Platinotype had been.

One leading question which is being addressed by the present investigation is: can Japine papers (§1.15) account for the observed surfaces of some of Stieglitz's Palladiotypes? Or do they involve additional coatings, as has been demonstrated by Constance McCabe in a wide-ranging investigation of his other work?⁴¹⁵ Further investigation by microscopy and infrared spectrometry, and direct sampling for chromatography/mass spectrometry, is being pursued to settle this point.⁴¹⁶ Stieglitz himself later complained of the cracking surface of "Palladio" papers⁴¹⁷ – a brittleness which may be symptomatic of the parchmientizing process. We also have the retrospective comment in 1978 from

his wife and model, the celebrated painter Georgia O'Keeffe, concerning the availability of platino- and palladio-type papers:

"After the First World War – platinum and other papers made before the war were not made anymore. No black surfaced paper was made at that time. Eastman developed quantity and gave up the idea of quality. The palladio prints were a very pale brown – very pale. They were on a beautiful parchment paper that was often dented in the shipping tube and had to be thrown away – while Stieglitz complained bitterly about it. But in time a darker brown paper was made – and finally there was a black palladio. It was better, but it was not in the same class with the black platinum paper that was made before the war." ⁴¹⁸

Another key question arises regarding Stieglitz's practice: did he use his potassium oxalate Platinotype developer to process his prints on Palladiotype paper? See §2.9. In the absence of any later publication or reference to his working methods, we must ask if he too ignored Willis & Clements instructions for Palladiotype citrate developer and clearing baths. There is some evidence from recent spectroscopic studies bearing tangentially on this question, as follows.

3.6 Elemental composition of Stieglitz prints

During the early 1990s, Constance McCabe and Lisha Glinsman of the NGA obtained the X-ray fluorescence spectra of many Stieglitz prints, which were presented to the *Stieglitz Colloquy* at the Center for Advanced Studies in the Visual Arts in 1993, and subsequently published.⁴¹⁹ They found evidence for the presence of both platinum and mercury in acknowledged "palladium" prints. It seems very improbable that Stieglitz would have recoated one type of commercial paper, Palladiotype, with different platinum and mercury chemicals – there is no evidence of his hand-coating at all, at this time (§3.5). The likely explanation for this finding is that the mercury and platinum in these images may have come from a used Platinotype developer, already on his darkroom shelves, which would have accumulated salts of platinum and mercury in the normal course of its previous use, and would chemically precipitate these metals into the palladium image during the development process. Most platinum printers kept and re-used their developing solutions for long periods of time – indeed, it was widely recommended to do so, because the solutions were thought to "mature" in some beneficial way – which was never quite specified chemically. This is still common practice – even a personalised ritual – among traditional users.⁴²⁰

There remains a difficulty over the chronology of some of Stieglitz's prints that contain both platinum and palladium: specifically, the portraits of Katharine Rhoades which are dated tentatively to 1915/16 – before the commercial production of palladium paper. Either the dates need to be re-evaluated, or the analysis implies that some manufacturers were already including palladium in their platinotype papers – without revealing so.

There is another strikingly anachronistic claim for early "palladiotypes": in Herbert Wendell Gleason's (1855–1937) photographic illustrations for a Bibliophile Society edition of Thoreau's *Walden* published in Boston in 1909.⁴²¹

This may be simply a case of misnamed platinotypes, on the part of the bookseller, but these items deserve examination by XRF, if still accessible.

3.7 Tonal reversal or "solarization"

Tonal reversal of the image shadows is clearly apparent in some of Stieglitz's palladium prints (see §6.18). The phenomena of partial image reversal and their historical uses have been quite comprehensively reviewed by photographic chemist, William Jolly,⁴²² who quotes Sarah Greenough on Stieglitz's use of the phenomenon after ca. 1919:

"... this clearly indicates that Stieglitz, once he discovered the effect, intentionally employed it for aesthetic purposes." ⁴²³

One celebrated Palladiotype by Stieglitz, mentioned above in §3.5, bears on the back of its mount a retrospective inscription in his own hand, dated 1939:

"Hands & Thimble - Georgia O'Keeffe 1920 by Alfred Stieglitz
-(Historical note): first use of solarization as an integral part of a picture." ⁴²⁴

This later "historical" annotation by Stieglitz, reclaiming retrospectively his priority to the discovery, may have been provoked by the work of Man Ray and Lee Miller in the 1920s, who claimed to be the first to use "solarization" for expressive artistic purposes, but they misnamed it thus, because these photographers were actually employing the Sabatier effect, caused by light-fogging the image during development.⁴ We may take it that, for Stieglitz around 1919, "solarization", or partial tonal reversal became a sought-after effect, for certain of his images at least. Palladiotype seems distinctly more prone to display the phenomenon than Platinotype, perhaps because printing-out occurs more easily with palladium salts due to their faster, more reactive chemistry (see §11.4 for a chemical explanation). Preliminary experiments (see §6.18) indicate that the effect may only be seen with dry sensitizers, at low Relative Humidity (RH<30%), and this experience may have caused Stieglitz to limit the days on which he was prepared to print, owing to the frequently high humidity prevalent at his holiday home at Lake George. Sarah Greenough, in her essay, "A Great Day for Palladio", has rediscovered the meteorological records for this area, and correlated the daily weather conditions with Stieglitz's remarks in his letters concerning the success of his print-making,⁴²⁵ and his deliberate employment of conditions of low relative humidity conducive to the "solarization" effect in Palladiotype. The following quotation from such a letter

⁴ *Etymological footnote 4: "tonal reversal" is the term preferred here to others that have been used to denote similar phenomena, such as "solarization, bronzing, split tone, or double tone". The effect seen here is not true overexposure "solarization" as it applies to the destruction of the latent image in silver halide photography, where the overexposure has to be in the order of 1000 times. Rather, the reversal apparent here is probably due to self-masking of the shadows by the image partially printing-out during the exposure, then augmented by a colour shift due to a difference in particle size when the remainder of the image is developed. Massive overexposure is not required to produce this effect.*

by Stieglitz conveys some sense of the importance he attached to the prevailing humidity:

"Weather is too perfect. So dry & clear that all vegetation is gradually going on the blink--burning up. So the weather is perfect. Great for palladioing but I'm not palladioing. I suppose I ought to order some by wire to let vegetation live. Rain would set in sure just as soon as the paper to be printed in "absolute dryness" arrived in the Lake George P.O. addressed to Alfred Stieglitz...." ⁴²⁶

3.8 Steichen's treatment of Stieglitz's Palladiotypes

Conservation problems with Stieglitz's Palladiotype *oeuvre* were recognised posthumously around 1946 by his widow, Georgia O'Keeffe, acting as executrix of his estate, assisted by her secretary, Doris Bry. How serious these problems were perceived to be can now be judged only from their comments based on their visual memories. O'Keeffe then entrusted at least 232 Stieglitz Palladiotypes from the 'Key Set' to the care of Edward Steichen (1879–1973), whom she believed could restore them chemically. In 1947 Steichen became Director of the Museum of Modern Art.

This whole episode has been researched in depth by conservator Douglas Severson, who quotes Bry from private conversations held in 1993–4, ⁴²⁷ describing the Palladiotypes as:

"...very, very yellow and gave you a feeling of disturbance."

When they were returned by Steichen, she said:

"...they came back looking clear and fresh...newly made again."

O'Keeffe herself was satisfied with the outcome at the time (1950):

"Steichen does something to them that clears them and to me it seems a good thing to do. I have just finished mounting a number from the key set that are very much improved. I trust Steichen to do this and I would not feel that way about anyone else. He thinks it will give the prints a much longer life." ⁴²⁸

Mystery surrounds Steichen's treatment post-1946 of the 232 Stieglitz Palladiotype prints from the 'Key Set'. Although Doris Bry questioned Steichen quite persistently, he remained silent on the nature of his procedure, so she and O'Keeffe simply made a record faithfully on the mattes of those prints which were annotated "Treated by Steichen". One or two rumours have since circulated about this undisclosed treatment: Rachel Danzig reports an interview with Richard Benson in 1985 in which he:

"...stated that Steichen reprocessed Stieglitz's prints with 1/60 parts HCl solution, then washed and rewaxed them." ⁴²⁹

Experiment shows that such a treatment of palladium images with hydrochloric acid of this strength would have 'reduced' the images perceptibly, so it seems unlikely to have been the procedure adopted by Steichen. From other sources, hearsay has suggested that Steichen treated them with "a strong solution of sodium acetate". This reagent could not have cleared the prints of

iron(III): sodium acetate solution is quite alkaline, and would have promoted hydrolysis. Recent experiments in re-creating and treating the stain (§9.5), together with XRF analysis, show that very little iron is actually removed by sodium acetate, but the intensity of the stain is diminished nonetheless, and a mechanism has been suggested (see §9.9 & §10.8) to account for this apparent 'clearing' effect.⁴³⁰ It has also been suggested that the name of this salt may have been mistaken for that of sodium citrate (*i.e.* the same as Willis's recommended developing and clearing agent for palladiotypes).

3.9 Problems of conserving Palladiotypes

There is now a growing suspicion that the "Steichenized" Palladiotypes have later re-yellowed once more, but it seems we have no qualitative evidence, such as photographs, for comparison. Is this again based on visual memories? Certainly many prints in this set are now far from being described as "clear and fresh", to recall Bry's words. The issue is complicated by the belief that many of Stieglitz's prints were coated with beeswax, which was removed by Steichen before his treatment, but not necessarily replaced afterwards. A few "untreated" Stieglitz Palladiotypes exist in various collections⁴³¹ which could serve as valuable 'controls', for comparison, if spectroscopic or colour measurement techniques could be brought to bear on them.

The further image degradation was first discovered by Douglas Severson in 1984 as a result of careful monitoring of a Stieglitz palladium print in the collection of the Art Institute of Chicago, one of several photographs sent to Japan for exhibition.⁴³² On the return of the item, optical densities were found to have increased by 30% in the mid-tones and 15% in the shadows. The cause of this change is uncertain: light levels may have been high at the exhibition venue, but it is suspected that while the work was in transit it was exposed to an outside atmosphere with a high moisture content.

Investigations have been carried out at the NGA in an attempted to reproduce the discoloration of Palladiotypes by accelerated ageing of simulacra, as will be described in §9.5.

3.10 Paul Strand's platinum prints

In 1931 the celebrated American photographer Paul Strand (1890–1976) is known to have approached the Platinotype Company with a request for them to augment their Platinotype paper with additional coatings so as to achieve a richer maximum density. "WBJ" paper resulted – Warm Black Japine. The history of this episode has been studied by Lisa Barro, and recently by Alisha Chipman. So far little has been discovered about this additional coating. In 2002 Barro reviewed the evidence for the exact nature of Strand's practice, and pointed out some inconsistencies in the various reports, as follows.⁴³³ Photo-historian Beaumont Newhall describes it thus:

"Until it went off the market in 1937, he preferred platinum paper... Strand used it to make brilliant long-scale prints. Not content with the quality of Japine platinum paper, which had a smooth semi-mat surface, he persuaded the manufacturers, the Platinotype Company of London, to produce double

coated paper, after demonstrating to them the improved results which paper so prepared by himself could produce." ⁴³⁴

Whereas, in his profile of Strand, Calvin Tomkins writes:

"Strand experimented with ways to deepen and enrich the tones even further, adding to the prepared paper a platinum emulsion he had made himself, and then gold-toning it to intensify the blacks." ⁴³⁵

In her studies of Strand's platinum prints by XRF, Barro found none containing gold. Only one has since been discovered by Stulik and co-workers in the J. Paul Getty Museum collection in 2013 (§5.9). Richard Benson, who printed with Strand in the early 1970s, is reported as saying:

"As far as I know, he only coated paper once. He talked to me about that at length. He brushed a platinum coating over a store-bought platinum paper so that he could make a print and send it to the company that made the paper to show them that their platinum content was too low. That was the only time he coated his own paper." ⁴³⁶

Alisha Chipman, while at the NGA in 2013, conducted an in-depth investigation of Paul Strand's *oeuvre*, and assigned his platinum prints to five categories, depending on the presence of the additional metals: lead, mercury, palladium and gold, as disclosed by XRF spectrometry. ⁴³⁷ The papers with a Japine surface, as indicated by microscopy and FTIR, are believed to include those specially doubly-sensitized by the Platinotype Company (so-called "WBJ") in response to a direct request from Strand, as described above. The finding of traces of palladium in the XRF of these by Matthew Clarke may be significant. Chipman also identified Ira Martin, the chief photographer at the Frick Art Reference Library, New York, as another important user of this paper, which was also shared by Alfred Stieglitz (§3.1), Ned Scott (§2.10) and Laura Gilpin (§3.12). Strand favoured the semi-glossy Japine surface papers in order to obtain more saturation in his blacks, and even went so far as to coat most of his platinum prints with a varnish. The subsequent discoloration and cracking of their surfaces now present problems to the photograph conservator, which are discussed at length by Chipman.

3.11 Composites with cyanotype and gum printing

A finished platinum print – on plain paper of the finest quality – is still receptive to over-printing with further photographic media. Thus, it is possible to make superimposed multiple prints which combine the characteristics of the platinotype or palladiotype with the same image rendered in other processes. The usual method is to print and completely finish the noble metal image first, because of the inertness of the image substance, then recoat the dry print with the other sensitizer, and make a second printing in register with the first using the same negative.

For a cyanotype over platinum or palladium the new cyanotype process is more suitable because it has about the same exposure scale as the platinotype or palladiotype process and a single negative will serve well for both printings; whereas the classical cyanotype process cannot render the density range of a negative made suitably for printing in platinum-palladium. ⁴³⁸ The reverse order

of process, with the cyanotype made first, is not rewarding with platinotype because of the effect of oxalate on Prussian blue: traditional platinotype developer will rapidly bleach and dissolve any Prussian blue image. On the other hand it should be possible with palladiotype because the recommended developer – acidified sodium citrate – will not attack Prussian blue (although it does render it light-sensitive). A cyanotype over palladium print was exhibited in 2016 by the Worcester Art Museum in their landmark *Cyanotypes* show: it was a print by Edward Steichen entitled *Jean Simpson in Profile* which is now thought to be of this type.⁴³⁹ XRF showed that the predominantly brown image is palladium, with iron detectable in small areas of residual cyanotype blue at the edges; the surface presents a slight sheen and a fine *craquelure* that suggests it may be a Japanese paper.

It is worth noting here that a degree of Prussian blue toning can also be imparted to a finished platinotype, without a second printing, by the catalytic toning procedure described in §9.13. This addition of blue to the highlights of a platinotype was sometimes referred to as a “Moonlight effect” toning, and could also be carried out by including potassium ferricyanide in a dilute oxalate developer with added glycerol.⁴⁴⁰

Platinotypes are also sympathetic to further elaboration by superimposing the printing method known as “gum bichromate”, which itself deserves a brief explanation here. An aqueous solution of gum Arabic (gum acacia) is used as a viscous binder for the chosen artists’ pigments, but is mixed with a soluble dichromate before brushing it onto the paper. On exposure to light through the re-registered negative, the chromium(VI) is photochemically reduced to chromium(III) which has the capability of partially insolubilising the gum by cross-linking its macromolecular structure, thus trapping a proportional amount of pigment in the hardened gum of those regions where the light falls. Excess pigmented gum in the lighter tones is subsequently dissolved away by washing in water to yield a negative-working process once known as “photo-aquatint”. The platinum tonality is thus enriched by the addition of a layer of colour in this ‘painterly’ but photographic method. The “gum over platinum” composite procedure still finds favour with some highly adept practitioners today.⁴⁴¹

On 15th February 2006, the world of photographic art was astounded by the sale of a single photographic print by Edward Steichen (1879–1973) for \$2.928M,⁴⁴² more than twice the previous record price paid for any photograph.⁴⁴³ Steichen’s print, entitled *The Pond – Moonlight*, dated from 1904, and was described as “multiple gum bichromate over platinum”. Here we have an impressionistic, dark landscape (on Long Island, apparently), illuminated by the moon rising between the boughs of a tree-lined, reflective pond – an evocative example of the romantic pictorial symbolism typical of the modernist genre, and so well-suited to the favorite medium of the day – platinotype. The print was sold at auction by Sotheby’s Holdings Inc., of New York, to an unidentified private collector.⁴⁴⁴ The vendor was the Metropolitan Museum of Art, New York, which had recently acquired the print among its purchase of the celebrated collection of the Gilman Paper Company,⁴⁴⁵ but the Met already possessed another print of this image, hence the decision to offer

the newly acquired one in this “landmark” sale. A third print from the same negative, but entitled *Moonrise – Mamaroneck, New York*, is in the collection of the Museum of Modern Art in New York; its process definition reads: “platinum, cyanotype and ferroprussiate print”. The redundancy in this description leaves some uncertainty about its accuracy in describing the actual composition. Steichen himself left a clue in an undated letter to Stieglitz:

“ Another one, Moonrise in three printings: first printing, grey black plat— 2nd, plain blue print (secret), 3rd, greenish gum. It is so very dark I must take the glass off because it acts too much like a mirror.”⁴⁴⁶

It is unclear to which of the three known, differing prints this remark refers.

The chief difficulty in multiple printing is maintaining registration between the successive images in the face of possible dimensional changes of the paper substrate when it passes through the cycles of hydroexpansion and contraction that accompanies multiple processes of wetting and drying. One technique for combating this problem is “pre-shrinking”, and another is to adhere the paper sheet to a rigid support, in the manner adopted by Irving Penn.(§4.1)

3.12 Platinum printers contemporary with Stieglitz

The work of other photographers who are also known to have used Platinotype Company papers could be potentially informative to this investigation, because they would have been obliged to confront the same problems of the “platinum famine” of 1916–20 at the same time as Stieglitz, and they may, for instance, have turned to Palladiotype papers. Their parallel practices and resulting prints are therefore likely to be of interest, as reference specimens of process, and some of their work may be more accessible for testing than very precious Stieglitz originals. The following candidates for this investigation have been identified so far, and brief summaries made of their contribution to the technical practice. A valuable overview of the role of precious-metal printing in early 20th century American photography is provided by Constance McCabe,⁴⁴⁷ who shows how several talented students of the Clarence White School became noted exponents of Platinotype (§2.11). These famous alumni include Gertrude Käsebier, Laura Gilpin, Margaret Watkins, and Anne K. Brigman. Together with Imogen Cunningham, all five women “carried the torch” for the platinum and palladium processes which were otherwise neglected during the ensuing years, some of them regularly hand-coating their own papers. On occasion this was at the price of some personal suffering, as related below.

Gertrude Käsebier (1852–1934) was known to hand-coat at least some of her own platinum papers, and recent XRF studies of a collection of her ‘platinotypes’ held at the J. Paul Getty Museum have revealed among them two pure palladium prints, believed to date from 1894 and 1896–99.⁴⁴⁸ All the other prints examined were found to be platinum prints containing mercury, but not all these are perceptibly sepia in colour, leaving an open question as to whether, in their making, the mercury was added to the sensitizer or to the developer.

Imogen Cunningham (1883–1976), was a celebrated American photographer and platinotypist who also had a background in chemistry, and showed interest in improving the performance of the platinum process by the addition of lead oxalate to the sensitizer.⁴⁴⁹ A short biography on the website of the Imogen Cunningham Trust says:

"Imogen Cunningham's thesis when she graduated from the University of Washington with a major in chemistry was titled "Modern Processes of Photography."

After graduation Imogen worked in the Seattle portrait studio of Edward S. Curtis, the photographer who produced the twenty volumes of "The North American Indian." Here she learned the techniques of platinum printing. In 1909 Imogen's college sorority, Pi Beta Phi, awarded her a grant to study photographic chemistry in Dresden.⁴⁵⁰ Her thesis, published in Germany, "Über Selbstherstellung von Platinpapieren für braune Töne," translates to "About Self-Production of Platinum Papers for Brown Tones." In this paper she urged the use of hand-coated paper for platinum prints, as much more convenient and easier to handle than commercial paper."⁴⁵¹

In an interview with Paul Hill and Thomas Cooper, Cunningham described how Gertrude Käsebier had become afflicted with platinum allergy:

"On your way back, you paid a visit to Gertrude Käsebier, didn't you?"

"Yes, I did. She was printing with platinum, and she had one eye covered by a patch, since she had gotten platinum poisoning. She had touched her face or eyes at some point when she was printing. I was always very, very careful. But some people are allergic to it, anyway. If you take up the paper, which has a powdery feel to it, and spread it around with your fingers, you can be sick."⁴⁵²

Mary Olive Edis (1876–1955)⁴⁵³ an Englishwoman, set up as a commercial photographer in Norfolk, England, around 1903, and became a leading society portraitist, and a commissioned war artist photographer during 1918–19.⁴⁵⁴ She made early Autochromes, but was also known to use Platinotype Company papers for her professional portraiture, which is abundant.⁴⁵⁵ She (more accurately, her printer, Lilian Page) was using these at precisely the same time as Stieglitz. Many of her portraits (over 400 of them may be seen in the English National Portrait Gallery⁴⁵⁶ and more in Cromer Museum⁴⁵⁷) are described as "sepia platinotypes"; five specimens of these were acquired from her remaining estate,⁴⁵⁸ for the NGA Photograph Conservation Study Collection, with the intention of subjecting them to spectroscopic and microscopical analyses. Some of these "sepia Platinotype" prints might be on Willis's "Japine" paper, to judge by their surfaces, but all so far investigated were found by XRF analysis to be platinum prints, with perceptible amounts of mercury present, but no trace of palladium.

Margaret Watkins (1884–1969)⁴⁵⁹ was born in Canada, and entered the Clarence White school in 1914 for a course of study, where she eventually served as registrar in 1920 and assistant instructor in 1922–3. Watkins then worked commercially in New York in portraiture, advertising, and fashion

photography. In 1928 she visited relatives in Glasgow, but the move there proved permanent, and her life became reclusive, although interspersed with photographically productive visits to France and Russia. After her death, the greater portion of her archive was inherited by her friend and neighbour in Glasgow, Joseph Mulholland, who has since curated and exhibited her work over several decades,⁴⁶⁰ and done much to elevate the reputation of this "nearly forgotten" photographer.⁴⁶¹ Her archive includes work by various students of the Clarence White School, whom she must have supervised, and can be seen at Mulholland's Hidden Lane Gallery in Glasgow. All her diaries and papers were donated by her legatee, Joe Mulholland, to McMaster University, Canada. There are also a number of her prints from 1919–1928 described as "vintage palladium prints" in the Robert Mann Gallery, New York.⁴⁶² Her palladium prints were almost certainly made on Willis's Palladiotype paper, and should repay investigation as examples of the medium.

Tina Modotti (1896–1942) was known to be a user of Platinotype until 1928, when she apparently gave up the medium and donated her remaining paper to Manuel Alvarez Bravo; he records that she also provided him with "her formula" for developing platinum prints.⁴⁶³ Curiously, the formulae for "Tina Modotti's developer for platinum prints" as quoted by Bravo, and for the "fixing bath", are identical with those specified by Willis & Clements and the Platinotype Company for processing *Palladiotype*. This strange transposition, the converse of most US practice, suggests that Modotti, who learned platinum printing from Edward Weston in Mexico ca. 1923, see §3.5, may have worked with Palladiotype papers, whence she acquired the developer formula. It is well-known that Weston himself favoured Palladiotype paper over Platinotype for his printing during the period 1917–23 (see below). Further investigation of Modotti's archive seems desirable.

Laura Gilpin (1891–1979) was born and raised in Colorado Springs, and was another distinguished alumnus of the Clarence White School in 1916–7, where, at the recommendation of Gertrude Käsebier, she acquired her skills in platinum printing from Paul Anderson. She made a living as a commercial photographer offering hand-coated platinum prints for their beauty and permanence – which continued until the 1970s, when the following interesting response by Gilpin was recorded by Hill and Cooper in their *Dialogue with Photography*:

"Today you are considered to be a master of platinum printing.

That is only because I kept doing it, and other people didn't. But the younger people who are doing it now have not discovered how to do a good black. This is something I want to look into. I think it's the light-sensitizer chemical. I think they have changed it chemically to make it last longer or something, because I have yet to see a good black.

Do you still coat your own paper?

I have done some recently ... " ⁴⁶⁴

Gilpin also devoted herself for sixty years to recording the landscape, history, and culture of her home region, the American south-west, compiling an unparalleled vision of Navajo life. Her archive is held at the Amon Carter Museum of American Art, Fort Worth, Texas.

Edward Weston (1886–1958) made quite extensive use of platinotype and especially palladiotype papers in the 1920s. There is correspondence between Alfred Clements and Edward Weston in 1921 to indicate that he and Clarence White favoured Palladiotype above all – fig. 3.1.⁴⁶⁵

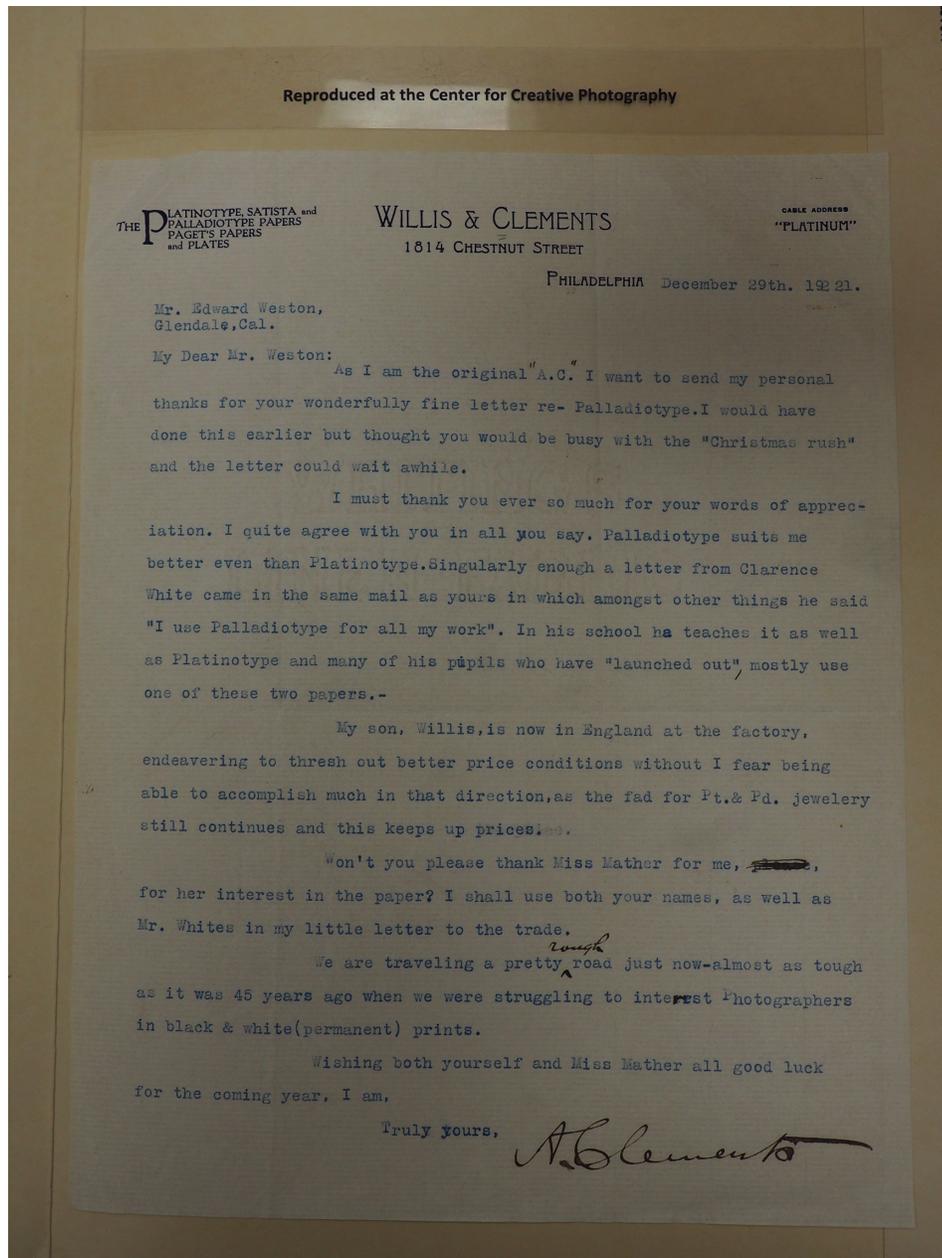


Fig.3.1 Letter from Alfred Clements to Edward Weston 1921
Collection of the Center for Creative Photography.

Weston's *Daybook* comments particularly on his use of the palladio paper on buff stock:

Dec. 23, 1925 – “One so easily gets into a rut. Why I have not used the white stock palladio before can only be answered by admitting myself addicted to buff from years of professional usage. And to use a tinted stock is a form of affectation near to ‘artiness.’ The white stock is clean, direct, unpretentious: it presents unveiled all the negative has to give. It reveals the best of a good negative and exposes the worst of a bad. There is no hiding behind a smudge of chemical color.”⁴⁶⁶

Margaret Wessling has studied the archive of Weston's prints at MFA Boston by XRF and found that a proportion of the palladium prints contained mercury.⁴⁶⁷ In view of the remarks by Tina Modotti, above, it raises the question: did Weston use his Palladiotype developer for his sepia Platinotypes also, or was the mercury deliberately added to the Palladiotype developer? If the latter, then what effect was he trying to achieve?

There have been numerous other distinguished artistic users of Platinotype and Palladiotype who, in contrast to those above, have not evidently concerned themselves with innovations over any technical aspects of the processes, so this technical history must be content only to acknowledge in passing the artistic contributions made to the medium by accomplished practitioners such as: **Anne K. Brigman** (1869–1950); **Alvin Langdon Coburn** (1882–1966); **Frederick Holland Day** (1864–1933); **Paul Outerbridge** (1896–1958).

4. Later 20th Century Platinum–Palladium Printing

Between 1940 and 1970 the practice of platinum printing sank to a low ebb, having been commercially displaced by the much less expensive silver–gelatin enlarging papers manufactured by the market–driven industry. In the early 1970s, a few photographic artists, especially those still working with large format equipment, began to rebel against this product uniformity by hand–sensitizing their own papers once more with platinum and palladium. They led a significant renaissance in the use of alternative photographic printing techniques, so that within a few years platinum–palladium printing regained its place as the supreme process, becoming the minority practice of an élite band of art photographers, who were prepared for such labour–intensive, costly work. In this era of extensively automated silver–gelatin printing, handmade photographs in platinum metals carried a certain cachet, and a correspondingly elevated price, and could claim greater permanence than the silver prints made with commercial materials.

4.1 *Irving Penn's initiative*

Following this interregnum of about thirty years, the practice of platinum printing was once again revitalized in the USA in the 1970's, by an initiative that originated with Irving Penn (1917–2009), the leading fashion and advertising photographer. He had been appointed in 1943 as a staff photographer for *Vogue* magazine, and for twenty years recorded in a very elegant style the celebrities, *fashionistas*, and public figures associated with the glossy magazine industry. But in the 1960s, as an expression of his discontent with the image qualities of the commercial half–tone printed page, Penn sought to renew his art through the medium of handcrafted platinum printing. His conversion to using platinum metals found its beginnings in his literature research in the New York Public Library in June, 1964, with the consultation of early journals and texts on the platinotype process, and by 1967 he could produce platinum prints that he deemed acceptable. For the next 25 years Penn committed himself wholeheartedly to the medium, both with new work and by personally reprinting images from his archive of negatives originally made for commercial publication, which were thereby transformed into independent and enduring works of art.

Penn first exhibited his platinum–palladium prints in 1975 at New York's Museum of Modern Art, under the ægis of the now–legendary director John Szarkowski. Penn's chosen subject matter for that body of work consisted of discarded cigarette ends ("butts") gathered from the streets of New York in 1972 by a studio assistant. In 1977 Penn followed this up with a similar exhibition entitled "Street Material" at the Metropolitan Museum of Art, New York, and at the Marlborough Gallery, New York. Such antithetical conjunctions of the lowliest subject–matter imaginable, subtly rendered in the most precious of all printing processes and exhibited at the most prestigious galleries of art in the country, naturally aroused considerable comment and aesthetic debate among influential critics, such as Alan D. Coleman and Michael Edelson.⁴⁶⁸ A complete set of the iconoclastic "cigarette butts" has recently been handsomely

published by Hamiltons Gallery of London in collaboration with the Irving Penn Foundation.⁴⁶⁹

Initially, Penn chose not to publish any details of his carefully researched and hard-won technical practice; however, over the years 1995–2005 he did deposit all his technical notes, together with many other studio materials, as the Irving Penn Archive in the Ryerson and Burnham Library at the Art Institute of Chicago.⁴⁷⁰ These records have been digitized and some are made accessible online.⁴⁷¹ The Department of Photography at the AIC also houses a collection of 134 master prints by Irving Penn,⁴⁷² which he donated in 1995.⁴⁷³

In 2002 Penn donated a further 83 of his platinum–palladium prints to the National Gallery of Art in Washington DC, together with 17 collages, entitled *Platinum Test Materials*, which he had assembled in 1989 out of the many and various trial–printings and numerous test–strips that he had accumulated as by-products of the making of his final prints. This collection of his work has been the subject of a scholarly publication by the Curator and Head of the Department of Photographs at the NGA, Sarah Greenough, who examines and expounds on the artist's motivation and achievement, based on her personal insights from conversations held with Irving Penn during 2003–4.⁴⁷⁴

During the initial period of his intensive experimentation with sensitizer solutions and papers, Penn soon discovered that the historical formulae he had adopted (see below) did not deliver maximum print densities and tonal ranges that satisfied his aesthetic tastes, as can be inferred from many of the trial pieces in his collages of *Platinum Test Materials*. Penn therefore chose to multiple-coat his papers in order to increase the final image density, which also enabled him to print a single image from several negatives, conveying more detail in different sectors of the tonal scale. He undertook a procedure characterised by re-coating, re-exposure and development, in order to build up density in the image layers.⁴⁷⁵ This procedure would have generated problems of dimensional instability in an unsupported paper sheet, because its hydroexpansivity would negate accurate re-registration for the multiple printings, but Penn overcame this difficulty by adhering each sheet of watercolour paper to a 'plate' of sheet aluminium metal, of 18 to 20 gauge, using Dupont's 'Surlyn A1650' thermoplastic adhesive.⁴⁷⁶ He also adopted an elaborate and precise pin register and punch system to ensure sharpness in the final image.⁴⁷⁷ The papers he used included Arches Aquarelle, Bienfang, Rives Bristol 100, Strathmore Carillon, and Wiggins Teape. By 1976, he had given up re-sizing these with the gelatin/alum he had used previously.

Penn also discovered that a mixture of platinum and palladium for the image produced results that were superior in quality to those of either metal used alone: platinum gave a good black but tended to coarseness; palladium was delicate but lacked density and tended to "solarise". Penn saw that a mixture of the two metals combined the virtues of both, as had been earlier advocated by E.J. Wall (§2.7). At an early stage, in the mid–1970s, he expressed his dissatisfaction with the quality of the ferric oxalate he could then obtain:

"The only Ferric Oxalate available to me (Amend Drug Co.) is brown. In spite of all the cautions in the old texts, the chemical houses know nothing of "bright green scales". The brown ferric oxalate works well, though it

sometimes leaves a heavy sludge in being dissolved and always requires filtration ..." ⁴⁷⁸

A detailed formulary for Penn's working methods has been compiled by Vasilios Zatsis, Associate Director of the Irving Penn Foundation,⁴⁷⁹ showing how Penn made up a set of stock solutions, following the traditional formulae quoted in Neblette's treatise of 1942,⁴⁸⁰ which were closely similar to those published by Anderson in 1937 and 1939 (§2.11);⁴⁸¹ both of these authors followed the original formulae published by Pizzighelli and Hübl in 1882 (§1.16).⁴⁸² These solutions were mixed to achieve contrast control by altering the amount of potassium chlorate in the sensitizer. Penn's practice was varied and complex, involving multiple negatives and printings to make a single image; however, for our limited purposes of comparison, we may confine our observations to Penn's standard full-strength sensitizer solutions that were made up from his four stock solutions, encoded as indicated in Table 4.1. ⁴⁸³

Sensitizer Component	Penn's Code	Substance as solute in water	Concentration % w/v (molarity)
Platinum	A	Potassium tetrachloroplatinate(II) 100 g in 600 cm ³ final volume	16.7% (0.40 M in Pt)
Palladium (concentrated)	3-2x	Sodium tetrachloropalladate(II) 100 g in 500 cm ³ final volume	20% (0.68 M in Pd)
Iron (normal contrast)	2	Ferric oxalate 210 g in 1000 cm ³ Oxalic acid 10 g	21% (0.9 M in Fe) 1%
Iron (high contrast)	2H	Ferric oxalate 210 g in 1000 cm ³ Oxalic acid 10 g Potassium chlorate 10 g	21% (0.9 M in Fe) 1% 1%

Table 4.1 Penn's main stock solutions for platinum-palladium printing

Penn recorded his multiple-coating mixtures and exposures on hand-written worksheets, but the numerical volumes of the stock solutions combined in his sensitizers are noted there without specifying any units, except in a few early (1967) sheets where both "drops" and "cc" were explicitly stated. A later typical worksheet of 1980,⁴⁸⁴ states that batches of sensitizer were mixed up, having a volume of 57 (and some of three times this, 171, for multiple prints). Considering the area that Penn coated, we conclude that the units for these volume figures cannot be 'numbers of drops' (each of volume *ca.* 0.05 cm³) because the volume of 57 drops would be impossibly small, *ca.* 2.8 cm³, for complete coverage of even a single sheet of typical area 50 x 50 cm (0.25 m²). Penn's volume units must be cm³, but this creates the problem that the entire volume of 57 cm³ seems impossibly large for a single coating of this area,⁴⁸⁵

which is apparently implied by the worksheets. This would correspond to a Specific Coating Volume of $228 \text{ cm}^3/\text{m}^2$, which is *ca.* 8 times the amount used in present practice (§6.10). It has been demonstrated practically that 57 cm^3 of dyed water *can* be worked into a paper sheet by persistent brushing and evaporation with a hot-air blower, but applying such a procedure to a genuine sensitizer solution would probably lead to extensive crystallization, which therefore makes this excessive coating volume seem rather implausible.

So the crucial question remains: “What area was this 57 cm^3 used to cover?” An answer is provided by Penn's explicit observation in an early worksheet that “28.5 cc barely suffices to coat 2 sheets 20 x 24”, and this observation is clearly repeated in one of Penn's notebooks in the Art Institute of Chicago archive.⁴⁸⁶ Now 28.5 cm^3 is exactly half of 57 cm^3 , which would therefore have just covered 4 sheets 20 x 24” ($51 \times 61 \text{ cm} = 0.31 \text{ m}^2$). This coating corresponds to a Specific Coating Volume of $46 \text{ cm}^3/\text{m}^2$. (For comparison, economical rod-coating requires a Specific Coating Volume of *ca.* $30 \text{ cm}^3/\text{m}^2$, see §6.10.)⁴⁸⁷ Moreover, for printing an edition it appears that Penn prepared his coatings in batches of three ‘plates’, which might explain why he chose the easily divisible number 57 as his standard batch volume, providing *ca.* 19 cm^3 for each coat of the three. This corresponds to a Specific Coating Volume of $61 \text{ cm}^3/\text{m}^2$, about twice the customary working value, but some of this volume may have been used for testing, on occasion covering four sheets.

On this basis, Penn's sensitizer chemistry become interpretable. For instance, his worksheets show that the standard sensitizer solution for his first ‘underprint’, of dimensions $50 \times 50 \text{ cm}$, was composed typically by mixing the four stock solutions as in Table 4.2:

Sensitizer Component	Penn's Code	Volume total/ cm^3	Volume / coat For 4 or 3 coats	Metal Amount in milliMoles/coat
Platinum	A	15	3.75 - 5	1.5 - 2 mM Pt
Palladium	3-2x	9	2.25 - 3	1.5 - 2 mM Pd
Iron (normal)	2	15	3.75 - 5	7.4 - 9.9 mM Fe total
Iron (high contrast)	2H	18	4.5 - 6	
Totals		57	14.25 - 19	3 - 4 mM (Pt+Pd)

Table 4.2 Irving Penn's typical sensitizer coating formula.

We see from these coating amounts that Penn used an approximately equimolar mixture of platinum and palladium, and sufficient ferric oxalate to provide a modest excess of iron(III) – about 25% – over the theoretical stoichiometry of $\text{Fe}:(\text{Pt}+\text{Pd}) = 2:1$ molar ratio. The resulting precious metal coating weight was $\sim 12 \text{ mMol/m}^2$ for a single coat spread over 3 or 4 sheets, approximately twice the amount used by Willis and others (see §5.1). Some of Penn's sensitizations also used an admixture of iridium salts, which is a platinum–group metal mentioned by Willis in his first two patents (nos. 2011, 2800), but so far no iridium has been detected in any resulting images.

Penn's developer was the customary one: 30% potassium oxalate with 0.5% oxalic acid. Clearing was in the traditional three baths of 1:64x diluted hydrochloric acid (37% w/v). As we have seen above, Penn favoured a heavy coating in order to achieve the densest blacks. The rather large volume of sensitizer that he soaked into the paper evidently generated difficulties with clearing the excess iron(III) salts; as Penn wrote in 1975:

“For a rich velvety black it is necessary to coat the paper quite heavily, brushing out the coating mixture for a long period of time. I believe that the heavy coating then requires a long time in the HCL [sic] to remove the residual iron. (6–10 hours seem to be what I require.)”⁴⁸⁸

He found that these very prolonged treatments in the dilute hydrochloric acid baths tended to cause density loss in his palladium–containing images and the disintegration of many of the fine–art papers that he tested. His final choice of paper favoured BFK Rives and Arches Aquarelle.

In a further endeavour to remove residual iron salts from the paper, Penn introduced a novel step in the processing: a “bleaching bath” of 5% sodium bisulphite after the hydrochloric acid clearing sequence. He noted that: “...the paper seems to whiten and generally clear...”. (This would have had the effect of reducing any residual iron(III) to iron(II), which is more easily removed from the cellulose; it is now a key step in the Malde–Ware processing sequence, see §7.22 and §10.10). Penn also placed great importance on a final deacidification bath to ensure archival permanence for the print, and he therefore employed the Barrow method of deacidification well–known to paper conservators, using solutions of the bicarbonates of calcium and magnesium.⁴⁸⁹

Penn's large, strikingly contrasty platinum–palladium prints, including still–lives, nudes, ethnographic studies and studio portraiture of celebrities and working people alike, are still widely exhibited, admired, and collected. They have established a 20th century benchmark for aspiring fine–art printers in platinum–palladium.⁴⁹⁰

4.2 Platinum–palladium revival in the USA

Contemporaneously with Irving Penn's celebrated productions in the medium, platinum–palladium printing began to be promulgated in the USA through publications by several other noted practitioners: George Tice (1970 and 1972),⁴⁹¹ Arnold Gassan (1977)⁴⁹², Nancy Rexroth (1977),⁴⁹³ William Crawford (1979),⁴⁹⁴ and John Hafey and Tom Shillea (1979),⁴⁹⁵ all of whom reiterated, in their essentials, the formulae and procedures published by Paul L. Anderson in

1937–8, see §2.11, which, we should remember, were in turn based on the ‘drop counting’ development process first devised and published by Giuseppe Pizzighelli and Arthur von Hübl in 1882, see §1.16.

During the 1980s, the alternative photography renaissance, which had begun in the USA, infused platinum–palladium printing with new life. Photohistorian Luis Nadeau has proposed five reasons for this contemporary revival:

- the decline of silver–gelatin printing,
- the wider acceptance of photography as art,
- the expressive range of the platinum–palladium medium,
- the relative ease of handcrafting the prints,
- increased teaching of photography in art schools.⁴⁹⁶

To supply the growing need for suitable materials, in 1976 Alan Goodman founded his company, *Elegant Images*, of Wilmington Delaware, and began providing Introductory packages of chemicals and paper for platinum printing. In 1981 the firm of Bostick & Sullivan of Van Nuys, California, was founded and published their *Labnotes and descriptive catalog of platinum and palladium chemicals and related products*. The leading platinum–palladium printer, Dick Arentz published *An Outline for Platinum Palladium Printing* in 1989, which became in later editions a respected text book *Platinum & Palladium Printing*, advocating procedures based on the products marketed by Bostick & Sullivan.⁴⁹⁷

The commercial production of palladium paper enjoyed a brief market re-appearance in the USA during 1988–93, launched by the Palladio Company of Robert and Sura Steinberg, although this venture proved lamentably short-lived owing to increasing difficulties with finding a suitable paper stock.⁴⁹⁸ In 1990, Dick Arentz persuaded the Cranes Paper Company to manufacture an alum–rosin sized rag paper specifically for the Platinotype process, but regrettably Cranes Platinotype did not remain on the market for long. In 1992, the master printer, Martin Axon, commissioned from the Arches Paper Company a paper specifically intended for platinum–palladium printing, called Arches Platine, which continues to be used successfully today and has undergone a recent improvement (2015).

Chemical supplies for alternative processes are now offered in the USA by Bostick & Sullivan, the Photographers Formulary, and Artcraft Chemicals. In 1997, Bostick & Sullivan launched a palladium printing–out process purchaseable in kit form, which was described in the photographic press as “brand–new”,⁴⁹⁹ and which they named “Ziatype” after an ancient Meso–American native sun symbol.⁵⁰⁰ This process strongly resembled the printing–out platinum–palladium method that had been published twelve years earlier in the UK (see below §4.3), but with the difference that some of the ammonium cation was replaced by lithium or caesium cations, based on the erroneous supposition that these cations would serve to control the humidity of the sensitizer. Unfortunately, this substitution imposes the limitation that Ziatype cannot make a platinum print – only palladium – because the presence of the lithium cation severely inhibits the printing–out of platinum (see §11.13) and, moreover, the caesium cation causes the crystallization of salts of low solubility, so requiring the sensitizer to be used hot.⁵⁰¹

4.3 *Platinum–palladium processes in the UK*

It is a British national irony that by 1939, use of the Platinotype process had completely died out in its birthplace, because photographers in wartime Britain were otherwise preoccupied, and found the expense of the precious metal and the large format negatives to be prohibitive disincentives to this luxury practice. Following the winding-up of Willis's Platinotype Company in 1937, British photography consequently entered a "platinum dark age" that was to last for over forty years.

It was as recently as 1982 that the photographic artist Pradip Malde, then based in Orkney, Scotland, and the present author, in Manchester, began their collaboration to devise an updated 'user-friendly' version of the process. Our re-examination of the platinotype and palladiotype chemistry from first principles led us to formulate a modernised print-out process resembling Pizzighelli's "direct printing platinotype" of 1887, see §1.16.⁵⁰² But we also employed some up-to-date chemistry in order to improve its accessibility, economy, and chemical reliability. This method was published in 1986, and taught in workshops at Paul and Angela Hill's 'Photographer's Place' in Derbyshire, and elsewhere, to those prepared to coat paper for themselves.

The full sequence of instructions for this process is set out in §7.⁵⁰³ This economic and highly controllable procedure did entail several innovations:

- The notoriously variable and unreliable ferric oxalate was, at the outset, rejected as the sensitizer for several obvious reasons (§11.2), and ammonium ferric oxalate, which is widely available commercially in consistently pure form, was adopted. The chemical argument for ammonium as the preferred cation for both platinum and palladium is set out in §11.13.
- Willis's time-honoured substance potassium tetrachloroplatinate(II) was not used as the source of platinum, because it may cause potassium ferric oxalate, which has only low solubility, to crystallise out of the mixed coating solution (§10.6). To avoid introducing potassium ions, we employed ammonium tetrachloroplatinate(II), which may be less widely available, but has the great advantage of being more soluble than the potassium salt, so this process can yield a good maximum density in one coat with a more concentrated sensitizer solution, and the trouble of double coating, with all its attendant difficulties, becomes unnecessary.
- Image colour from this print-out platinum–palladium method can be varied over a range of browns to neutral grey by altering the proportions of the two metals and by regulating the relative humidity of the coated paper, if necessary, in a humidifying box before exposure (§11.16).
- In place of the traditional brush or foam-rubber applicator, in 1986 the author and Pradip Malde introduced the more economic coating instrument, the glass coating-rod, which has since gained wide acceptance among alternative printers. However, it is said "there is nothing new under the sun", and we have since discovered three historical references from the 1850s to the use of glass rods for coating photographs, suggesting that it was then standard practice!⁵⁰⁴ Glass

spreader rods are kinder to the paper surface, avoid contamination and ensure economy and uniformity in coating the very expensive sensitizer (§6.10, §7.16).

- On some papers, coating and absorption of the sensitizer was assisted by the use of a non-ionic surfactant, called Tween 20 (§7.15).
- A carefully sequenced wet-processing treatment with disodium EDTA, followed by sodium sulphite (in Kodak Hypoclear), and then tetrasodium EDTA, was employed to effectively clear the residual ferric iron (§10.10).

These were some of the innovations introduced into the contemporary context of platinum-palladium printing in order to provide a reliable and reproducible method of printing-out. Examples of artistic work made by means of this version may be seen on Pradip Malde's web pages.⁵⁰⁵

Due to the changes in the industrial methods of manufacturing fine papers in the 1980s, which leave the paper composition in an alkaline condition (§8.6), most commercial fine-art papers then became inimical to the chemistry of all siderotype printing. A serious need arose during the 1980s for a suitable paper – in earlier years it had still been possible to obtain papers that were not alkaline-buffered. To this end Ruscombe Mill, in collaboration with the author, produced their 'Buxton' and 'Herschel' papers specifically designed for the siderotype processes, as is described in §8.7.

Platinotype also saw some reacceptance in other European countries: for the Francophone world, the Swiss magazine *Camera* in its February 1979 issue published a complete description of the traditional platinum process in French by Carlos Richardson, but the process never gained great popularity there, as the leading contemporary French exponent of platinum-palladium printing, Jean-Claude Mougín, observes:

"Nevertheless the platinotype wasn't quite successful in France where the photographers used to prefer the carbon, Artigue and Fresson processes."⁵⁰⁶

The platinum renaissance did find a following in Sweden, especially aided by Björn Anderson's account of the instructions in Swedish,⁵⁰⁷ and there are noted users now in France, Germany, Italy, and Australia. Throughout the world today, there has grown a significant constituency of practitioners of palladium, and mixed palladium-platinum printing, including commercial print studios,⁵⁰⁸ but there are now very few workers who can successfully accomplish printing in pure 100% platinum.⁵⁰⁹

4.4 Impact of digital imaging

In the last two decades, photographic practice has seen digital imaging technology, with its piezoelectric ink-jet printers, substantially replacing the analogue photochemical methods using silver-gelatin materials, which trace their traditional origins back to the 19th century. In this age of digital lens-based media, it is salutary to remember that analogue chemical photographs – negative or positive – when properly processed, are permanent repositories of visual information in a robust format that is easily handled, stored and retrieved as enduring, flat objects. Their complete independence of any prevailing digital computer technology – or its possible sudden lack – ensures that well-prepared

platinum–palladium prints on fine paper will remain humanly readable, without any obvious time limitation. Such prints could endure for a millennium. This union of the noblest of metals with the commonest organic substance on earth also provides artists with a satisfying embodiment of ‘being true to their materials’. This contrasts with digital images which have been translated electronically into strings of binary code stored on relatively fragile media such as compact discs or computer memory chips. It is hard to see how machine–dependent, digitally–encoded images can ever lay claim to ongoing robustness and accessibility. Digital photography does, however, provide a useful facility by enabling the making of large internegatives without a darkroom, and today many alternative photographers prefer such a hybrid practice. They employ digital techniques to print large negatives by ink–jet onto transparent film, as described in Appendix IV, then use these negatives to print positives in platinum or palladium upon a substrate of the finest cellulose paper.

The large–scale demise of the traditional practice of silver–gelatin negative photography with archivally–processed silver prints will prove a great loss to many historical photographic archives. Although ink–jet printer pigments are improving in their stability, they will never match the platinotype, unless platinum and palladium salts themselves are used as the piezographic printer's ‘ink’. This desideratum suggests the following innovative – but still entirely hypothetical – ink–jet practice. It is hoped this will soon be realised practically.

4.5 Digital chemitype or chemical piezotype

The basic proposal of what might colloquially be called ‘metal–jet printing’ is to use a digital ink–jet printer with its ink replaced by a solution of a suitable chemical, to deliver a ‘potential image’ onto paper. This would consist of a simple substance, for instance potassium tetrachloroplatinate(II), or sodium tetrachloropalladate(II). Once dried into the paper fibres, the potential image is developed by a direct chemical reaction with another suitable solution, for instance a powerful reductant such as hydroxylamine or hydrazinium chloride, which can precipitate the stable, insoluble image substance, such as platinum or palladium metal, within the paper fibres, in proportion to the coating weight of the metal salt laid down by the printer. A simple wash in water would remove the excess chemicals, which are all soluble, resulting in a *chemical piezotype*. A platinotype made by this means should be fairly indistinguishable in its chemical and physical structure from a genuine platinotype made by the hybrid digital–electromechanical/analogue–photochemical route.

Some hybrid photography practitioners have already gone part–way towards this idea with the suggestion of loading an ink–jet printer cartridge with an alternative photographic sensitizer solution, e.g. a platinotype mix, then printing out a digital image electromechanically, exposing it uniformly to strong UV light to form the platinum metal image, processing in the usual wet developer and clearing sequence, and thus make a platinum print without the need for any internegative. Although this procedure has been proposed, this author is not aware that it has ever been carried into practice.

What I wish to emphasise here is that making platinum prints *photochemically* from ink–jet printed negatives is quite unnecessary, because

digital chemitype makes the optical analogue printing step redundant, and offers a huge simplification of the usual hybrid practice. Given direct chemical methods of forming the image, a door is suddenly opened onto a wide range of possible new image substances, instead of the very narrow choices hitherto imposed by photochemical imaging, which has always been restricted effectively to platinum, palladium, silver, gold, Prussian blue, and the artists' pigments incorporated in the dichromated colloid processes.

Besides greatly widening the range of possible image substances, the necessary chemicals and their 'development' by redox or metathetical reactions, could be very simple. For instance, the 'ink' could simply consist of a soluble salt or complex of *any* of the platinum metals (ruthenium, rhodium, palladium, osmium, iridium, or platinum, plus rhenium) or coinage metals (copper, silver, or gold), or even the less electropositive heavy metals such as mercury, thallium, lead or bismuth, any of which are reducible. Other obvious possibilities would be the precipitation of highly insoluble inorganic pigments such as the sulphides, selenides, chromates or iodides of metals such as zinc, cadmium, mercury, silver, barium, lead, bismuth, etc. Even cyanotype could be duplicated simply by filling the printer ink cartridge with potassium ferrocyanide solution (cheap, non-toxic, non-corrosive) and developing the potential image in a dilute bath of any iron(III) salt (e.g. the sulphate, chloride or nitrate). Other highly-coloured ferrocyanides of, for example, copper(II) and uranyl(VI) ion could be similarly generated. Preliminary experiments, conducted simply by imbibing the solutions into paper, drying, then immersing them in the reagent bath, have yielded deposits of metal and pigment having good colour and optical density.

Hosts of other possibilities for this kind of chemical imaging will suggest themselves to the inventive 'metal-jet' printer-chemist, for example the electroless deposition of a non-noble metal such as nickel, cobalt, or chromium onto a catalytic potential image formed in palladium (§4.8). The scope for new archivally stable image substances of various colours, chemically generated on plain paper, is huge, and it is possible that full 3-colour printing systems might be devised, as well as the monochrome precious metal and pigment images.

The research and development needed to bring this idea to actuality would have to resolve technical issues which are no doubt already well-understood by the experts in the rheology of ink-jet printing: the formulation of suitable additives to impart the appropriate viscosity and surface tension to the 'jetted' solution, so that it is optimised for accurate imaging and adequate penetration of the cellulose paper fibres, without 'feathering'. Doubtless these are deep commercial secrets, already well-understood by the manufacturers of printer inks. The practice would call for a dedicated ink-jet printer, and special precautions against print-head corrosion may be an issue with some chemistry, but a benefit would come from the 'ink' being a true solution, not a particulate suspension, so there would be no problems of clogged printheads.

This proposal offers some very strong cost-saving economic advantages:

- It would eliminate all the alternative photographic paraphernalia: no UV light sources, printing frames or vacuum easels, coating implements, safe

lighting, photosensitive chemicals, etc. This might encourage more digital photographers to try 'alternative' image substances and fine papers.

- It would eliminate the large internegative – which is costly in specialised ceramic-coated film and pigment printer inks.
- The wet processing procedure would be simple, reusable, economic, and eco-friendly, generating minimal chemical residues. The shorter time to production of the final print would also enhance the commercial potential of this form of photographic printing, for commissions which could guarantee image permanence.
- Most importantly, there would be no wastage of the precious metals, like platinum, that might be employed. Analogue photochemical printing is grossly wasteful: in making an average platinotype, about 94% of the precious metal coating is washed away, and only about 6% remains as image substance in the paper, because a print of an average scene is about four stops (16 times) less in total metal density than the maximum black for which the entire paper sheet has been coated. So by laying down on the paper with an ink-jet printer just enough platinum salt to make the image, one would save 16-fold on the raw cost of precious metal required at present, because none is washed away in the processing. Saving about 94% of the cost of platinum, palladium, silver, or gold would be a significant benefit which could greatly widen the appeal and use of these precious metals as print media.

If the objectives of this proposal were achieved, it would challenge the two main claims to uniqueness of prints made by traditional hand-crafted photographic siderotype processes: namely, the permanence of the image substance and the aesthetic qualities of the matte paper print surface. The logical end result of a successful digital chemotype project would be the disappearance of our present hybrid practice of making digital negatives for alternative photographic printing: the photochemistry would be rendered quite superfluous. The major area of appeal would therefore be to the present practitioners of the hybrid processes, but its ease and simplicity might open the door to a wider constituency of digital photographers, and there could also be commercial market applications in specialized security printing and archival images.

4.6 Describing platinum and palladium prints

In §4.1 and §4.2 of this chapter, we saw how the blending of platinum with palladium, first mentioned in §2.7, has today become a standard practice, in the search both for economy and ease of printing to the highest quality; but this mixing of the two metals may have some unfortunate and undesirable consequences. Among those of the alternative process community today who profess to make "platinum prints", there are regrettably a few who have become rather lax in their description, because their platinum solution is mixed with an excess amount of palladium solution, so the resulting prints probably contain only 10% to 20% platinum at best (which is precipitated more slowly than palladium – see §11.5). To draw a commercial analogy: it would be considered fraudulent to describe as 'gold', jewellery which actually consists of 90% silver. The chemical analogy is exact: palladium (Pd) bears the same relation to

platinum (Pt) as silver (Ag) does to gold (Au). From the relevant part of the Periodic Table of the Elements, at the end of the three transition metal series, it can be seen that all four metals are adjacent:

Fe	Co	Ni	Cu	Zn
Ru	Rh	Pd	Ag	Cd
Os	Ir	Pt	Au	Hg

This little polemic is not intended as a condemnation of present practice, but a plea for transparency and truthful labelling in the future. Dealing with precious metals carries certain ethical obligations in their description, hence the elaborate system of jewellers' hallmarks for silver and gold, legally administered by Assay Offices – and this system extends to platinum and, in some countries including the UK, to palladium.

In the early 20th century, photographic manufacturers such as William Willis of the Platinotype Company made a clear distinction between their platinum and palladium papers, and this distinction persisted as late as 1979, in the seminal handbook by William Crawford, who only mentions mixing the two as an afterthought. Considering the present day practice of indiscriminate mixing of the two metals, it is desirable that some obvious guidelines should be followed in describing the resulting art works so that collectors, curators and gallery directors will not be confused or misled. It is also vitally important for conservators to know the composition of the image if there is any possibility of conservation treatments being applied to the objects in the future, because palladium has a greater chemical vulnerability than platinum. The following guidelines are suggested:

- A print made with only a palladium salt as the precious metal source should be called a *palladium (Pd) print* or a *palladiotype*.
It must be noted that the addition to the sensitizer of a drop or two of so-called "Na2" – a meaningless, but commonly-used abbreviation for sodium hexachloroplatinate(IV) Na_2PtCl_6 used for contrast control in one version of the process – does not qualify the resulting image as a "platinum" or even a "palladium-platinum" print. There will be no platinum in it, because "Na2" is not significantly reduced to platinum by iron(II) oxalate.
- A print should only be described as a *platinum (Pt) print* or a *platinotype* if it has more than, say, 90% platinum content as its image substance. This is a figure open to debate, but is here suggested by analogy with "22 carat gold", which contains 91.6% gold by weight, and is generally acceptable as a "gold object". A lower figure might also be argued as acceptable: "18 carat gold" contains 75% gold by weight.
- The commonest practice today is to mix platinum and palladium salts in the sensitizer – in proportions that vary widely from one practitioner to another, and are rarely disclosed. This presents the greatest uncertainty in description, because the relative amounts of the two precious metals in the final print will not be the same as they were in the mixed sensitizer applied to the paper; the image will always be deficient in platinum. Salts of platinum(II), as used in the process, are slower and more reluctant to be reduced to the metal than are the salts of palladium(II) – several factors affect these relative rates of reaction, as discussed in §11. This effect has

been clearly demonstrated recently by the noted platinotype printer and photographer Ian Leake.⁵¹⁰ If the image contains platinum as the dominant (>50%) component it may be called a *platinum–palladium (Pt–Pd) print* or a *platino–palladiotype*, but this proportion is unlikely to result unless the ratio of metals in the original sensitizer was Pt:Pd > 2:1. If palladium is the major component, which is the general practice today, then it should be named with appropriate priority as a *palladium–platinum (Pd–Pt) print*, or *palladio–platinotype*.

A useful addition to the terminology has been suggested by Pradip Malde:

“I prefer to use the term ‘platinum/palladium’ as a general way of denoting all recipes using either one or both of these metals. The hyphenated form, ‘platinum–palladium’ is used by me to describe a print made from a combined recipe of platinum and palladium salts, where the greater portion of metal in the finished print is platinum, or platinum and palladium are present in almost equal amounts. By this logic, prints where palladium is the predominant ingredient should be called palladium–platinum.”

4.7 Identifying platinum prints

For the ultimate proof of composition of the image substance, there is no substitute for X-ray fluorescence spectrometry, see §5.5, but the requisite equipment is expensive. In trying to identify a platinum–palladium print by more humble means – the unaided human eye – the characteristics to look out for may be briefly described as follows – (with the exceptions in parentheses):

- a perfectly matte paper surface showing no reflective glare from any binder layer (but 'Japine' papers, §1.15 and §5.7, show a slight sheen. Some practitioners coated their platinum prints with beeswax, etc.);
- surface paper fibres are visible under a lens (but are not obvious in 'Japine' papers, where the cellulose surface has been reconstituted);
- colour varying from neutral grey–black to rich sepia brown;
- no trace of image fading (although some mercury–toned platinotypes may be an exception, due to the loss of volatile mercury);
- the possible presence of pale yellow or straw–coloured staining – probably due to residual iron(III). (This may also occur in other siderotype processes, such as kallitype.)

While the ultimate criterion for identifying a print must rest with analysis of the image substance itself by X-ray fluorescence (XRF) spectrometry (§5.5), which is non–invasive, there is a simple chemical method of detecting platinum in an image, which is "only a very slightly invasive test":

- Place the smallest possible drop of hydrogen peroxide solution, 6% H₂O₂ ("20–volume") in a dark region of the print, and examine it with a lens.
- The presence of platinum in the image will cause tiny bubbles of oxygen gas to form in the drop, which quickly becomes opaque.
- If the platinum is present in substantial proportion, the drop will be seen to effervesce quite vigorously, evolving oxygen gas. Pure palladium prints will not respond to this test.

The only other product of this platinum-catalysed decomposition is water, so this slightly invasive test should not cause any permanent damage to a platinum or palladium print after the drop has been blotted off with a cotton-wool bud or other absorber. It could, however, damage other less robust prints, or compound images such as gum-platinum, and is not recommended for very precious items.

4.8 Deposition of metals on palladium images

During the 1970s, the catalytic properties of palladium were employed to enable processes for printing images more economically in a range of non-noble metals. A “latent image” of palladium at a very low coating weight (ca. 20 mg/m²) was first printed by means of an iron-based sensitizer, then greatly intensified through its catalysis of the electroless deposition of a non-noble metal from a metastable solution of the metal ions in the presence of a strong reducing agent.⁵¹¹ This procedure had long been known in silver photochemistry, specifically the calotype process, where it used to be termed “physical development”; although it is no less “chemical” than conventional development; it also parallels some of the catalytic toning procedures adopted for platinum images – see §9.13.

Typically, the photosensitizer may consist of a very dilute solution of a tetrachloropalladate(II) (ca. 0.1%) and trisoxalatoferrate(III) (ca. 2–4%). The light exposure produces a “latent image” of palladium nanoparticles which is then treated in a bath of nickel(II), cobalt(II) or copper(II) chloride salts, (ca. 4%) containing also a strong reductant such as sodium hypophosphite (2%), NaH₂PO₂, to precipitate the non-noble metal catalytically onto the palladium image. As the authors affirm:

“... the use of nickel, cobalt or a mixture thereof has produced outstanding images which have excellent black rendition and which are very stable.”⁵¹²

Such a system tends to produce images characterised by high contrast, suitable only for ‘line’ or ‘half-tone’ applications. However, it was found that lower contrast continuous-tone images may be obtained if the developer bath also includes salts of antimony, bismuth, tin, lead or titanium.⁵¹³ The stability and longevity of images made by these means does not yet appear to have been tested.

5. Analysis of Platinum Papers and Prints

William Willis never disclosed his formulations for the final version of his 'cold development' Platinotype papers first marketed in 1892, which were highly successful commercially and most widely employed from that year on. He did not seek a patent, and no Platinotype Company records in the UK are thought to have survived the second World War. Uncertainties about the composition of his papers are steadily being resolved by historical research and recent chemical and spectrographic analyses of unexposed Platinotype papers from the early 1900s, as will be described below.

Likewise, the formulation for Willis's first commercial Palladiotype paper in 1917 was not published either, and there is no patent for it or any relevant publication. The only presently-known sealed tin of unexposed Palladiotype paper, dated 1937, is in the collection of the Museum of the History of Science, Oxford,⁵¹⁴ but specimens have not been made available for analysis. Until the composition can be confirmed the best assumption is that, by analogy with his Platinotype paper, Willis probably employed ferric oxalate (aka iron(III) oxalate) and sodium tetrachloropalladate(II) as his sensitizer.

5.1 Willis's formulae

Willis's patents for Platinotype may be taken as a guide to composition – a complete transcript of all six patents is provided in Appendix VI, thanks to Ian Leake – and they are consistent with the quantities cited in Willis's first publications – see §1.6 and §1.7. In Willis's earliest patent no. 2011 of 1873, the ferric oxalate (60 gr/oz) and potassium chloroplatinite (10 gr/oz) solutions were separately coated onto the paper, so no exact quantitative inferences can be reliably made from them. In patent no. 2800 (1878), the same constituents were premixed to give a sensitizer solution with 65 gr/oz ferric oxalate and 15 gr/oz potassium chloroplatinite, but the developer also contained 7 gr/oz potassium chloroplatinite, so some indefinite amount of the platinum was supplied from the developer. In patents nos. 1681 (1887) and 16,003 (1887), the ferric oxalate (60 gr/oz) was applied alone to the paper and all the potassium chloroplatinite was contained in the developer at 9 or 10 gr/oz.

However, in patent no. 1117 (1880) Willis states that he used a single solution for coating, containing equal concentrations (60 gr/oz) of the two ingredients. This coating solution, containing 60 grains of the platinum salt potassium chloroplatinite (K_2PtCl_4 FW 415.11) per fluid ounce, has a concentration of 136.8 g/l of the substance, and is 0.33 molar in Pt. (For conversions of units see Appendix VIII). The identical weight of ferric oxalate converts to a concentration of 0.57 molar in Fe, assuming a formula of $Fe_2(C_2O_4)_3 \cdot 6H_2O$ FW 483.84. (The degree of hydration can vary – some sources say $\cdot 5H_2O$ with FW 465.83, which would give a solution 0.587 molar in Fe.)

Furthermore, in patent no. 1117, Willis also states that his paper contained "between 1.7 and 4 grains of K_2PtCl_4 per square foot", preferring the latter value. If that value may be taken to refer to his most concentrated '60 grain' platinum solution, then Willis's specific coating volume would have been $4/60 = 1/15$ fluid ounce per square foot. This converts to $20.4 \text{ cm}^3/\text{m}^2$, which is

broadly consistent with the specific coating volumes of sensitizer commonly applied today – see §6.10. The range of Willis's coating weight converts to 1.19 to 2.79 g/m² of K₂PtCl₄ or 2.86 to 6.72 mMol/m², which corresponds to a platinum metal coating weight of 0.557 to 1.311 g/m². The low end of this range is in agreement with quantitative XRF analysis of unexposed platinotype paper from the American Aristotype Company, dated 1903, which is reported to have a platinum coating weight of 0.66 g/m², corresponding to 3.38 mMol/m².⁵¹⁵

These quantities imply a molar ratio of Fe : Pt of 0.58 : 0.33 = 1.76 : 1 in a sensitized layer produced with Willis's most concentrated sensitizer. It is, perhaps, surprising that Willis's patent should specify maximum quantities which fall short of the theoretical chemical stoichiometry of 2 : 1, but errors in the textbooks of the day suggest that there was at the time some lack of clarity concerning the formula weights (relative molecular masses) of platinum compounds.⁵¹⁶ In Willis's sensitizer at the minimum of the platinum concentration range, the Fe : Pt molar ratio would be ~4 : 1, so the theoretical value of 2 : 1 does fall within the range he specifies, assuming that the iron concentration is held constant.

Recently, Matthew Clarke at the NGA has made more extensive quantitative elemental analyses for platinum and iron in specimens of unexposed papers from the Platinotype Company and others, which throw fresh light on this problem, see §5.5.⁵¹⁷ He finds platinum metal coating weights of 0.518 and 0.611 g/m² for Willis's "KK" and "AA" papers, respectively.

5.2 Sources of paper rawstock

Willis did not reveal the source of the paper rawstock that he used as a base to coat for his commercial Platinotype papers, but there are some clues about its nature from various sources. British-made fine rag papers of the nineteenth century employed gelatin as the sizing agent, which was sometimes called "glue" or "animal sizing", and the fine papers from Whatman's Turkey Mill in Maidstone, Kent, especially, were the natural choice for Talbot's early silver photography in the 1840s; but gelatin, then of variable quality, is often inimical to platinum printing, as Willis soon discovered, so it was necessary for him to look elsewhere, abroad, for his paper supply.

By the 1860s, and for several decades thereafter, only two paper mills in the world were capable of manufacturing grades of paper high enough in quality to fulfill all the requirements of photographic processes.⁵¹⁸ Already by 1851, the French firm of Blanchet Frères et Kléber, whose papermills were located in the town of Rives near Grenoble in south-eastern France (Isère), had earned a worldwide reputation for the purity of their photographic rawstock. The only other significant manufactory was the German company of Steinbach & Co., of Malmedy, in Rhenish Prussia, which was famed for its photographic paper base, the so-named "papier de Saxe", and where Willis is said to have visited in the 1880s.⁵¹⁹ Certainly by 1882, 'Saxe' was the paper Willis was using, according to Henry Baden Pritchard's account of his visit to the Platinotype Company, hosted by Willis's partner, H.B. Berkeley:

"Mr. Berkeley is good enough to accede to our wish. "This, you see, is a roll of paper as we receive it," he says. Since it is a roll some five feet broad and a yard or two thick, there is no difficulty about seeing it, and we at once say so. "Only Saxe paper is employed, and this comes direct from Steinbach," and then Mr. Berkeley proceeds to say how it is prepared for platinotype purposes." ⁵²⁰

The importance of an appropriate sizing agent for Platinotype printing was recognised by Willis from an early stage, and there was some discussion of it in the photographic literature of the 1880s. Regarding the sizing agent, the following quotations by W.H. Harrison are significant:

"Mr. Willis says that he avoids gelatine, and as a substratum uses starch."

Captain Pizzighelli and Baron Hübl intentionally or unintentionally avoid gelatine, their paper being 'sized' at the mills with 'resin' ... That several platinum salts exercise a coagulating power upon certain colloids is known, and Sir Humphry Davy was ... the first to make known the fact..." ⁵²¹

However, by 1896 a mixed size of arrowroot starch and Nelson's gelatin (possibly a purer variety than that usually employed by papermakers) was being recommended for the self-preparation of platinum paper.⁵²²

The paper favoured by Pizzighelli was made by Gustav Röder & Co. at Marchendorf Mill, and their paper was called "ivory vellum". Pizzighelli also warned that:

"Handmade paper (water colour) sized with animal glue ... seriously hinders the reduction of the platinum" ⁵²³

Baron Arthur von Hübl makes the following observations (in this translated passage from his original 1895 treatise):

"The following types of paper are recommended unreservedly for platinum printing: The smooth and unglazed Rives and Steinbach papers are very pure, substitute-free rag papers for photographic purposes. They are engine-sized and perfectly usable for all methods of platinum printing. The handmade paper No. 27 of the Neusiedler Company for paper production in Vienna is also a very pure handmade paper, sized solely with resin soap, having a smooth grain and is very well suited for larger images. The rolled drawing paper of Schleicher & Schüll in Düren is a relatively inexpensive paper, of beautiful surface, engine-sized and recommended for very large formats.

The English watercolor papers from Whatman and from Zander, then the Harding-paper, are characterized by a particularly fine grain, and for this reason are very popular for platinum pictures. Unfortunately, these types of paper, as already noted, are animal-sized, and can therefore only be bad for platinum printing, in certain cases, one is compelled to desize them and then perform a fresh resizing with a more suitable binding agent." ⁵²⁴

The German paper used by the Platinotype Co. was described by George Dawson in 1880 as:

"Saxe ... prepared by the makers specially to give pure whites, as nearly all other papers contain substances which combine with platinum salts, thus

producing impure highlights. With other papers too it is impossible to produce good halftones." ⁵²⁵

This author also observed that since carbon dioxide gas was evolved, colloidal binders were unsuitable.

The Platinotype Company and Willis & Clements offered the platinotype sensitizer solution for sale, together with a paper suitable for hand-coating which was probably resin- or arrowroot-sized:

"...these substances have certain advantages over gelatin, which is coagulated by the salts of platinum, and is apt to work in streaks." ⁵²⁶

Willis's paper rawstock was imported into the USA in bulk by the agents, Buchanan, Smedley and Bromley, of Philadelphia. The paper base, described as "made expressly for the process", but not otherwise identified, was retailed as "Solar Paper" by Willis & Clements by the sheet,⁵²⁷ or even wholesale in rolls of 50 or 100 yards and 54 inches wide!⁵²⁸ But it was evidently also being offered for sale more widely by the importers as a paper well-suited for a whole range of artistic purposes, as can be seen from their advertisement of 1886:

"The best artists and solar printers in the United States and Europe use Platinotype Paper for large and small pictures. This paper is manufactured for Willis & Clements' Platinotype Process, and is the purest and most desirable grade of paper made in the world for ink, crayon, or pastel. Samples free. Buchanan, Smedley & Bromley, Importers, 1030 Arch St., Phila." ⁵²⁹

There is some evidence that this was the "Papier de Saxe", No. 174, manufactured by Steinbach & Co. in Germany, expressly for Willis, who had spent some time there commissioning a paper to suit his purposes.⁵³⁰ Thus, around 1892 in Jerome A. Barhydt's handbook on *Crayon Portraiture*, it is stated that a special Steinbach paper was the rawstock used by Willis for the previous nine years:

"The process was first introduced by Mr. Willis in 1874, and he has since made improvements. He claims that the platinotype paper does not contain any animal sizing. The early experiments convinced him that the paper upon which the image was to be printed would prove an important factor as all photographic paper contained animal sizing, which was found to be antagonistic to platinum salts. The action of platinum salts upon a paper containing animal sizing gave it a tint which no amount of acid washing could remove. For the past nine years Mr. Willis has had manufactured for his special use a Steinbach paper, free from the animal sizing, and he also uses a cold developer, thereby causing the paper to retain its original elasticity." ⁵³¹

Later, the Platinotype Company appears to have turned to the French-made papers from Rives which, like the German papers and in contrast to the British ones, were not sized with animal gelatin but usually with arrowroot starch and resin, and those produced by Blanchet Frères et Kléber at Rives were widely recommended and employed later as Platinotype papers.⁵³² The company records of BFK Rives show sales to the Platinotype Company starting as early as 1887. Evidence also comes from John Tennant, the editor of *The*

Photominiature, who recommended Rives N° 74 in 1899,⁵³³ and the same paper was recommended in *The Process Photogram* in 1896,⁵³⁴ and by A.J. Jarman in 1904 and 1907.⁵³⁵ In a retrospective article in 1929, E.A. Salt, a long-term employee of the Platinotype Company stated that:

“The paper, of beautiful surface and colour, is the finest product of the famous Rives’ Mill... nor is there any gelatine present.”⁵³⁶

In 1898, the rival French and German paper companies, Rives and Steinbach, joined forces, until 1914, establishing The General Paper Company in Brussels to market their products, including Eastman Kodak among their customers. In their studies of historical photographic papers, Sarah Wagner and Cyntia Karnes have pointed out that in the process of forming this cartel their prices immediately doubled. This increase was a blow to platinum paper manufacturers because their product was already more expensive than silver, making them even less competitive. In 1898, the Rives watermark changed, with two stars added to BFK Rives and it was renumbered as No 75, instead of No 74.⁵³⁷

This monopoly stimulated a number of other German papermakers such as Felix Schoeller of Osnabruck, to try to produce a paper suitable for photography (by then, mainly albumen printing).⁵³⁸ Papers recommended at the time included: "Schopf papier No. 27" from Neusiedler A.G. Papier-fabrikation, Vienna, and roll drawing papers of Schleicher and Schüll, Düren.⁵³⁹

Visible watermarks on historic Platinotypes are very rare, but in one archive of over 200 British topographical Platinotypes – made between 1892 and 1901,⁵⁴⁰ and *probably* on Willis's Platinotype paper – one print was noted by the author bearing the watermark "BFK Rives N° 75", the new watermark adopted in 1898. It would be helpful to have a detailed specification for these Rives papers that were supplied by Blanchet Frères et Kléber, if they were indeed the rawstock for Willis's later products. A French history of the Rives paper company refers to a catalogue of 1911 which is said to list 60 'numbered' types of non-baryta paper.⁵⁴¹ This reference, if it could be found, might lead to an insight into the paper composition.

A comprehensive specification of papers for photographic purposes, mainly silver-based but mentioning platinum, with some details of testing methods and a summary of practices current in 1904 may be found, translated from the Italian and reprinted in *Wilson's Photographic Magazine*.⁵⁴² There Dr. M. Scava of the Royal Italian Industrial Museum reports the results of his analyses of the photographic papers of Steinbach and Rives:

"Dr. Scava says that he analyzed some samples of this paper (namely, that made by Messrs. Steinbach & Co., of Malmedy, Rhenish Prussia, and Messrs. Blanchet, Frères & Kléber, of Rives (Isère), France), at the laboratory for testing paper at the Royal Italian Industrial Museum. The approximate percentage of used flax was 85, and that of new cotton 15. The sizing was resin and starch mixed. The resistance to crushing, measured with a Schopper dynamometer, was slight, considering the nature of the pulp, which had a short fibre and was worked; the average elongation was 24 per cent, and the average length of rupture, 2500 metres, estimated with a

Schopper dynamometer in an atmosphere containing 65 degrees of moisture (Regnault hygrometer). The humidity of the paper was about 6 per cent; the percentage of ash was 3 to 4 per cent, and in some instances ran as high as 9 to 14 per cent, being composed essentially of kaolin and baryta."

In 1919, as a consequence of World War I, the city of Malmedy was annexed to Belgium by the Treaty of Versailles, and it is now in the Province of Liège, still home to the Steinbach Company and a National Paper Museum.⁵⁴³

5.3 Pizzighelli's formulations

Pizzighelli's "direct printing platinotype" of 1887 (§1.16) departs from the traditional mould in making use of sodium or ammonium ferric oxalate as the sensitizer instead of ferric oxalate. For chemical reasons explained in §11.2 this results in a substantially printed-out image, provided that the paper has been allowed to acquire some humidity. Pizzighelli published three recipes,⁵⁴⁴ but they are all essentially similar. His basic formulation used four stock solutions, **A B C D**, in Table 5.1 converted into modern chemical units (Appendix VIII).⁵⁴⁵

Soln	Substance	Proportions	% w/v	Molarity
A	Potassium tetrachloroplatinate(II) (K ₂ PtCl ₄ FW 415.11)	1 part in 6 water	~15.6	0.376
B	Sodium trisoxalatoferrate(III) (Na ₃ Fe(C ₂ O ₄) ₃ .3H ₂ O FW 442.93)	40 parts in 100 water	~34.1	0.77
	Sodium oxalate (Na ₂ C ₂ O ₄ FW134)	3 parts in above	~2.56	0.19
C	Potassium chlorate (KClO ₃ FW 122.55)	0.4 parts in 100 parts B	~0.4	0.033
D	Mercuric chloride 5% solution (HgCl ₂ FW 271.5)	20 parts	1.67	0.061
	Sodium oxalate 3% solution	40 parts	2	0.15

Table 5.1 Composition of Pizzighelli's platinotype sensitizer solutions

Pizzighelli recommended mixing the stock solutions in volume ratios:
For black tones: **A : B : C** = 5 : 6 : 2. For brown tones: **A : C : D** = 5 : 4 : 4

The final concentration of platinum in the mixed sensitizer is ~0.15 molar.

Solution **C** serves only to increase the sensitizer contrast for negatives with an inadequate density range, and causes a deterioration in quality. It now seems an unnecessary complication to use it, especially with step tablets, which have more than sufficient density range. So the recommended simplified mix for black tones becomes:

A : B = 5 : 8, which corresponds to a molar ratio Pt : Fe = 1 : 3.3.

Sodium trisoxalatoferrate(III) is not readily purchasable, unlike the ammonium salt. Solution **B** can be prepared by dissolving 21.15 g of sodium

oxalate in 100 cc of warm water and adding in small portions 21.85 g of ferric oxalate powder with stirring until all is dissolved.

Pizzighelli's other variations on this basic formulation contained glycerol as a humectant for use in very dry environments, and gum arabic presumably to 'improve' the surface qualities of the print. These seem to be undesirable additional variables, which only complicate testing the process at this time.

In 1907, A.J. Jarman published his similar recipe for a platinum paper intended for "water development", which also employed gum arabic, and several other apparently superfluous ingredients such as lactic acid and oxalic acid.⁵⁴⁶ When a formulation contains as many as eight ingredients it becomes very improbable that their proportions can have been experimentally optimised, or even that the necessity for each component has been clearly demonstrated, and such recipes may reasonably be viewed as deriving from the "eye of newt and toe of frog" school of chemistry.⁵⁴⁷ Jarman's formulation had two other defects: instead of sodium or ammonium ferrioxalate it recommended the use of a commercial solution of ferric oxalate, then obtainable and defined only by its hydrometer reading on an unspecified scale.⁵⁴⁸ The formula also has an inadequate amount of extra oxalate to convert the ferric oxalate entirely to ferrioxalate anion, which would not work well without an oxalate developer. He also specifies a potassium tetrachloroplatinate solution which (at 1 part in 12 of water) is less than half the usual strength. With all the additions, the final concentration of platinum in Jarman's mixed sensitizer is estimated to be 0.071 molar. This should be compared with the value for Pizzighelli's "direct printing" sensitizer above, of 0.15 molar, and the value for the standard "development" sensitizer (§6) of 0.225 molar. Jarman's version has recently been tested and found, unsurprisingly, to yield rather feeble results in maximum optical density,⁵⁴⁹ despite his bold published claim:

"The color of these prints will be of a very rich black".

5.4 Sizing agents in Willis's papers

To help NGA scientists elucidate the composition of Willis's later commercial paper, the author has supplied unopened sealed specimens of original unexposed Willis Platinotype papers, types KK and AA dating from ca. 1906, which are known to be among those employed by Stieglitz.⁵⁵⁰

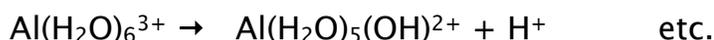
Preliminary spot tests on unused specimens of the KK paper had previously indicated the presence of alum-rosin sizing agent.⁵⁵¹ This tentative observation has now been confirmed by instrumental analysis using Gas Chromatography and Mass Spectrometry (GC-MS) at the NGA by scientist Christopher Maines:

"Using pyrolysis and gas chromatography with mass spectrometry, and in situ methylation by TMAH, we determined that the Platinotype KK paper contains rosin. Fortunately, we were easily able to "split" the paper and analyze the sensitized side separately from the rest of the paper. The only organic component detectable by this method in the sensitized side of the paper is rosin."⁵⁵²

The only carbohydrate was glucose (the monomer from cellulose and starch). GCMS analysis could not confirm the presence of starch as the iron and

platinum salts in the paper interfered with the analysis.⁵⁵³ However, an iodine spot test using 5% w/v iodine and 10% w/v potassium iodide in water (Lugol's Solution) performed by Sarah Wagner at the NGA showed the presence of starch in KK, AA, and Japine papers, indicating that these Platinotype Co. papers were sized with alum-rosin-starch and did not contain a coating of protein as had been previously hypothesized.

Historically, alum-rosin internal sizing, also called 'engine' sizing, was carried out during beating of the paper pulp,⁵⁵⁴ before formation of the sheet, by addition of an alkaline solution of rosin, called rosin soap, containing the sodium salt of the diterpene, abietic acid, which is water soluble.⁵⁵⁵ The pulp is then acidified by treatment with alum (potassium aluminium sulphate), which forms hydrogen ions by hydrolysis of the hydrated aluminium(III) cation:



causing the precipitation within the fibres of the insoluble, hydrophobic diterpene, abietic acid (Fig. 5.2),⁵⁵⁶ for which the aluminium ions also act as a mordant to the cellulose.

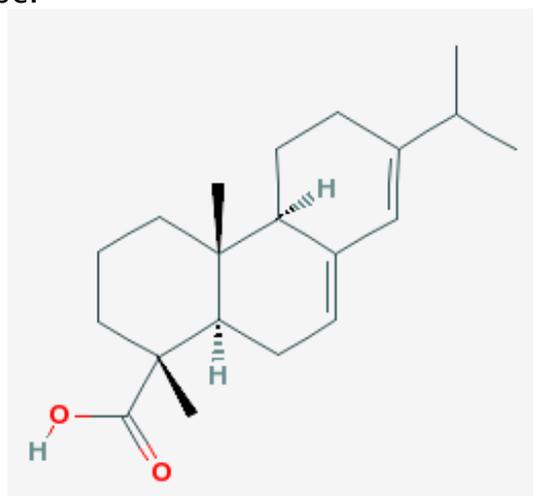


Fig. 5.2 Sizing agent abietic acid

5.5 X-ray spectrometry

It was not until the 1980s that curators and conservators became sufficiently confident that the application of X-Ray Fluorescence spectrographic analysis, abbreviated to XRF, was indeed non-destructive and non-invasive, so that the technique began to be tentatively applied to photographs, including platinum and palladium prints.⁵⁵⁷ Analytical samples such as photographs, which present a very low metal coating weight, require the instrument to be operating near the limits of its detection capability, so tend to produce XRF spectra suffering from low signal-to-noise ratios, and some consequent uncertainty in their interpretation. Nonetheless, valuable photohistorical results began to accrue, and in the early 1990s an XRF study of Alfred Stieglitz prints at the National Gallery of Art by Constance McCabe and Lisha Deming Glinzman disclosed many important features of their composition and led to the re-attribution of process details in many cases which had been wrongly identified by visual inspection alone – see §3.6.⁵⁵⁸ These researchers also discovered the importance of using

both molybdenum and barium secondary target anodes to generate X-rays of wavelengths for optimum sensitivity in detecting both platinum and palladium.

An alternative technique of X-ray spectrometry is made possible by an adaptation of the electron microscope, in which the electron beam generates the characteristic X-rays which are detected and analysed; it is called Scanning Electron Microprobe – Energy-Dispersive X-ray analysis or SEM-EDX. It has the advantage of being able to detect light elements, because the sample is held *in vacuo*, but for the same reason it is limited in application to small specimens.

For easy reference in examining XRF spectra, it will be convenient to tabulate here the energies of the characteristic X-ray lines of the significant metallic elements occurring in photographic prints, in ascending order of energy, using the customary notation and units of kiloelectronvolts (keV):

	Z	M α	M β	M γ	L α	L β	L γ	K α	K β
transn		4f-3d	4f-3d	4d-3p	3d-2p	3p-2s	4d-2p	2p-1s	3p-1s
Fe	26							6.40	7.06
Pd	46				2.8	3.1	3.5	21.18	23.82
Ag	47				2.9	3.2	3.7	22.16	24.9
Ba	56				4.5	4.9	5.8	32.0	36.3
Pt	78	2.0	2.1	2.3	9.44	11.07	13.5	65.9	76.7
Au	79	2.1	2.2	2.4	9.7	11.5	13.8	~69	
Hg	80	2.2	2.3	2.5	9.9	11.8	14.2	~71	
Pb	82	2.3	2.4	2.6	10.5	12.5	15.3		
U	92	3.1	3.3	3.5	13.5	16.5	20.5		

Table 5.2 Energies of the characteristic X-rays of elements in photographs

In 1989 a specimen of the Platinotype Company's KK paper, from a previously unopened tin dating from 1906, was examined by Scanning Electron Microprobe-Energy Dispersive X-ray analysis (SEM-EDX) by Dr. Ashok Roy, Head of the Scientific Department of the National Gallery, London. See Fig. 5.3. The following elements were detected and their suggested origins are:

Aluminium	Al	alum (potassium aluminium sulphate) sizing hardener
		aluminosilicate (clay paper filler)
Silicon	Si	aluminosilicate (clay paper filler) e.g. kaolinite
Platinum	Pt	potassium tetrachloroplatinate(II) sensitizer
Sulphur	S	sulphate in alum or gypsum (calcium sulphate)
Chlorine	Cl	potassium tetrachloroplatinate(II) sensitizer
Potassium	K	potassium tetrachloroplatinate(II) sensitizer; alum
Calcium	Ca	paper additives: chalk (calcium carbonate); gypsum
Iron	Fe	ferric oxalate sensitizer
Copper	Cu	paper impurity? Brass from blades of Hollander beater?

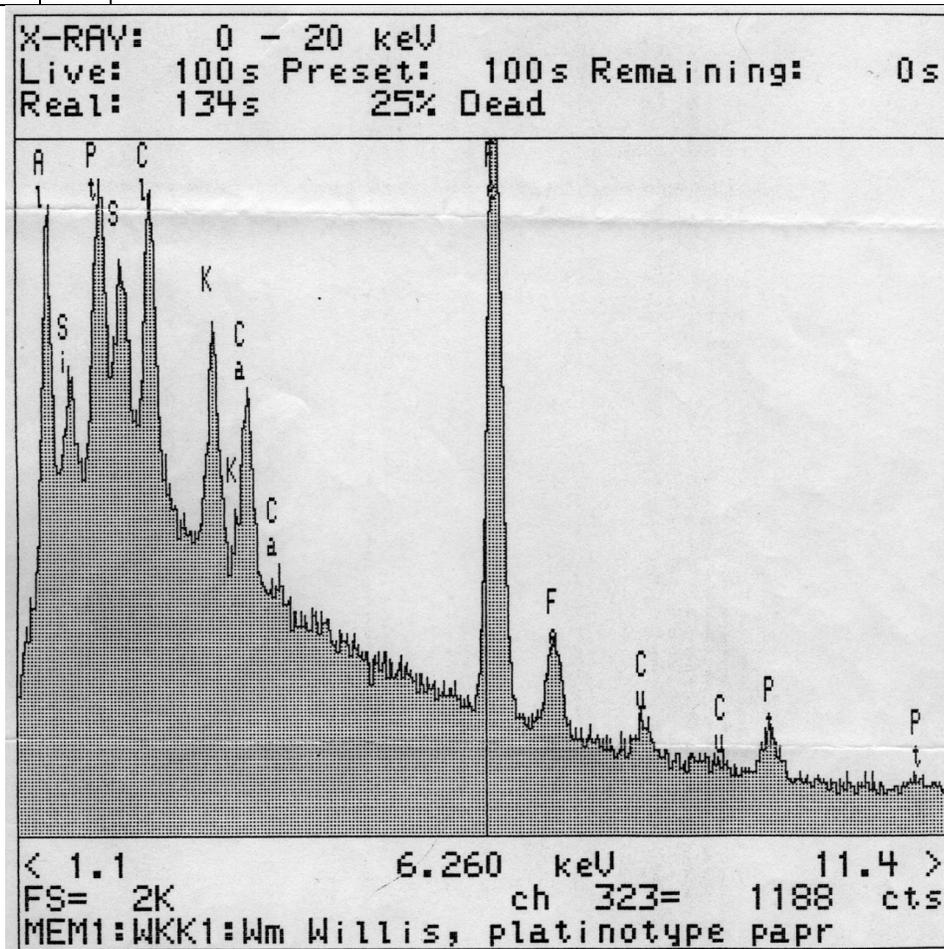


Fig. 5.3 EM/EDX Spectrum of Willis's "KK" Platinotype paper, ca. 1906.
 Courtesy of Dr. Ashok Roy, Science Department, National Gallery, London, 1989

The same paper was later examined by X-ray fluorescence spectrometry (XRF) by Jacqueline Rees at the Victoria & Albert Museum, London, in 1993, (Fig. 5.4) and the metals zinc (probably as white pigment) and lead (Willis's additive) were also discovered to be present at very low levels.⁵⁵⁹

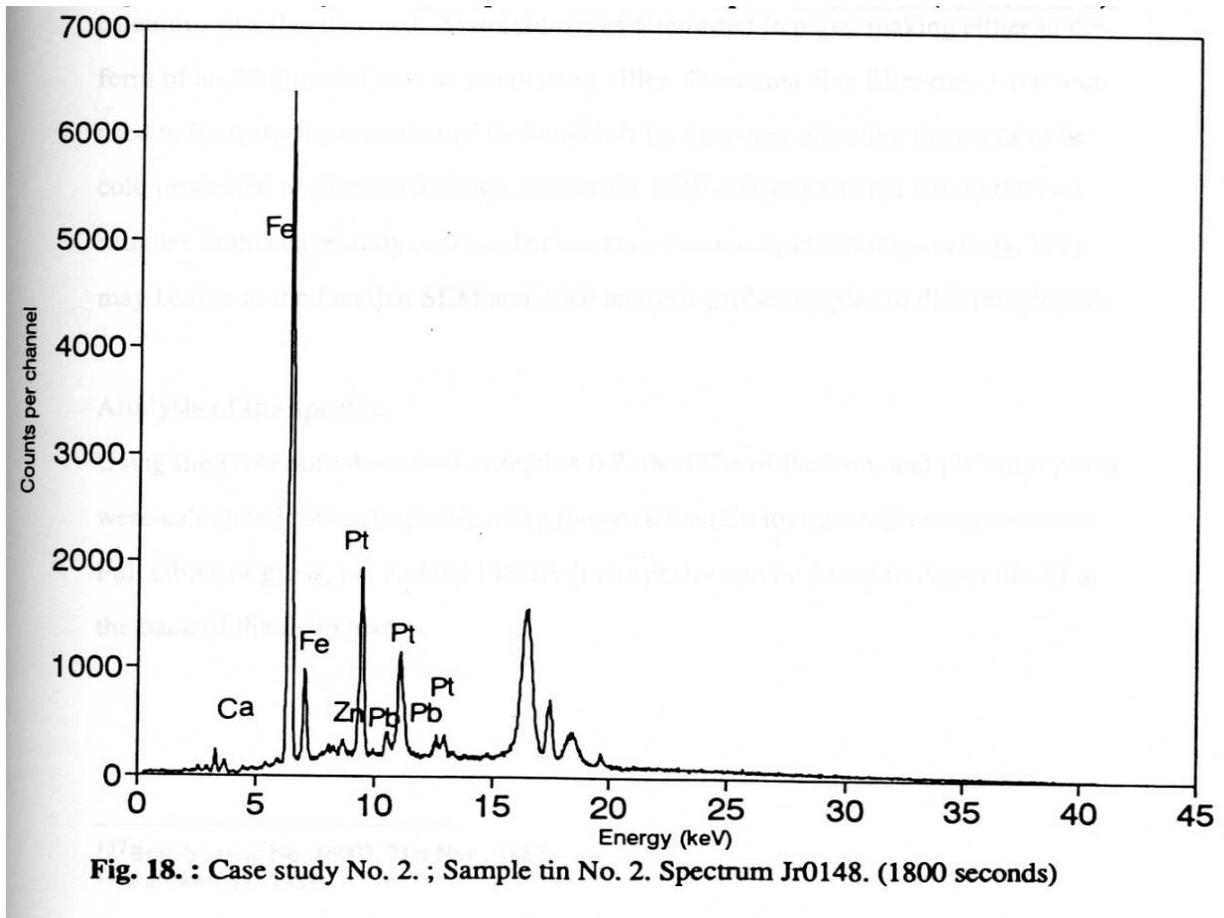


Fig. 5.4 XRF Spectrum of Willis's "KK" Platinotype paper, ca. 1906
 Courtesy of Dr. Jacqueline Rees, Victoria & Albert Museum, London, 1993.

In 2011 the same paper was again examined by XRF (Fig. 5.5) by Matthew Clarke at the NGA, and traces of the additional elements chromium, possibly a contrast-control agent, and barium, possibly as baryta pigment, were detected, Fig. 5.5.

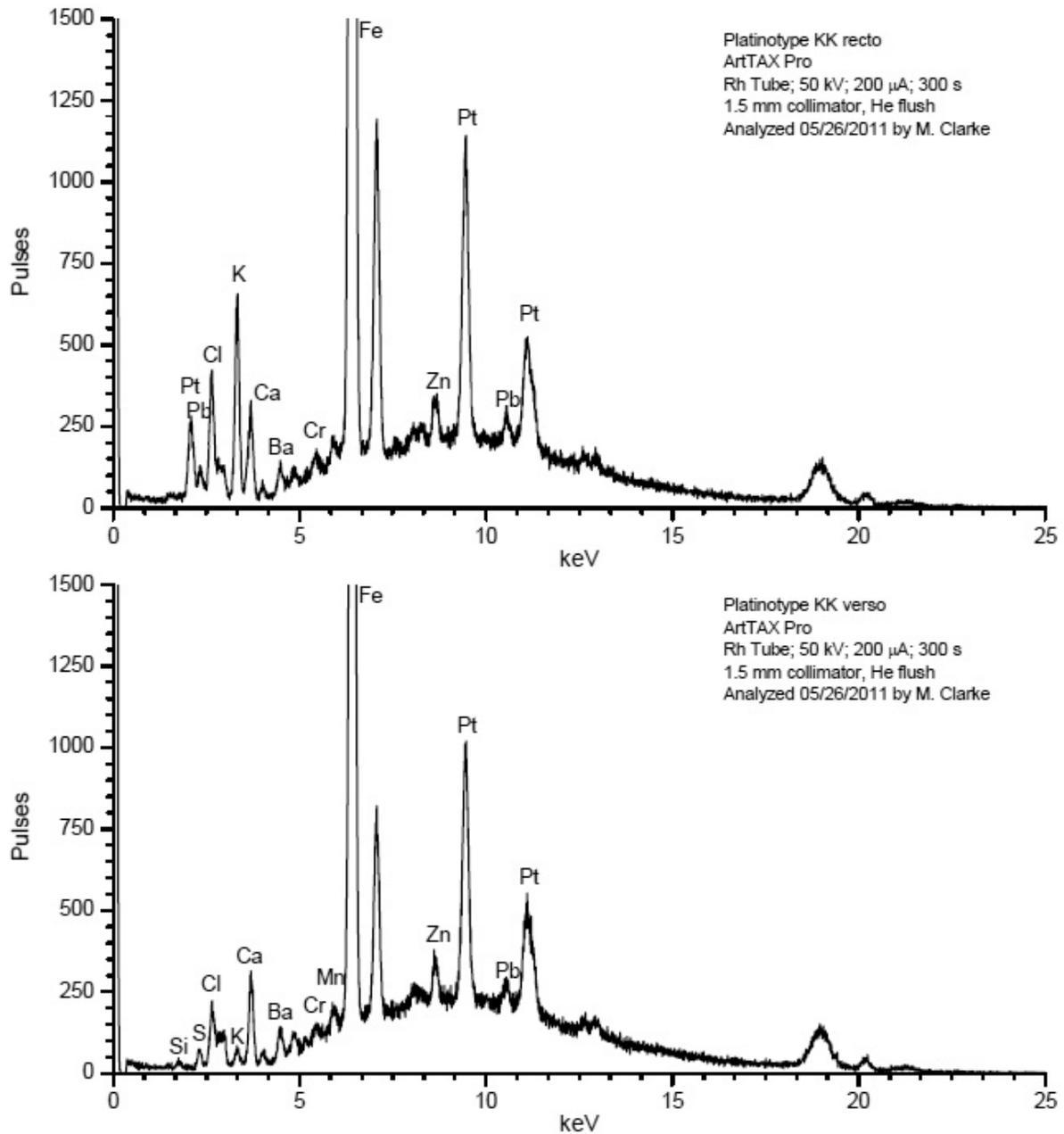


Fig. 5.5 XRF spectrum of Willis's "KK" Platinotype paper, ca. 1906
Courtesy of Dr. Matthew Clarke, National Gallery of Art, Washington, 2011.

Clarke has taken the XRF technique further by performing quantitative analyses for platinum and palladium in test prints and correlating the observed metal coating weights with the measured optical densities of the image, obtained at various relative humidities, as shown in fig. 5.6. The sensitizer used here was a Malde-Ware printout formulation with Pt:Pd=1:1 (molar).

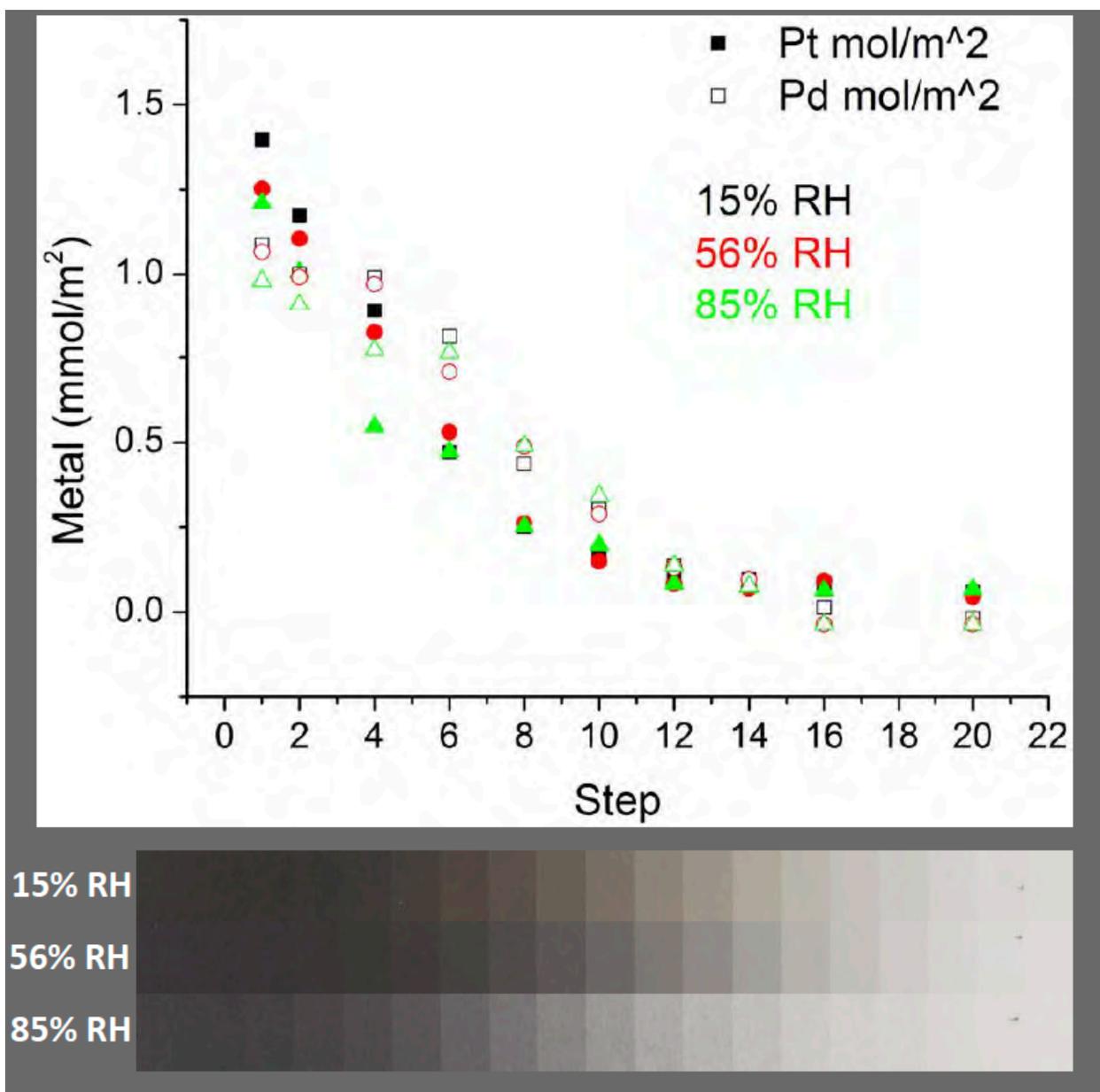


Fig. 5.6 Pt and Pd coating weights as a function of optical density and RH

Courtesy of Matthew Clarke et al

Some early platinotypes are found by XRF to contain, in addition to the elements listed above, cobalt and arsenic in the paper substrate. This signals a paper containing smalt – a blue pigment that was added historically in papermaking to ‘whiten’ the paper and combat yellowing, as mentioned in §1.12.⁵⁶⁰ Smalt is a cobalt potassium glass, finely ground, and a more stable blue pigment than ultramarine or Prussian blue for this purpose, although it has the disadvantage of being abrasive, and a reputation for blunting quill pens. Although the nominal formula, $K_2CoSi_3O_8$, shows no arsenic, the presence of this element can be understood if the cobalt glass was made from one of the common cobalt ores, smaltite $CoAs_2$, or cobaltite $CoAsS$, without preliminary roasting to the oxide.⁵⁶¹

5.6 Infrared and Raman spectroscopy

Infrared spectrometry over the customary region of 4000 – 650 cm^{-1} provides information on the characteristic frequencies of vibration of functional groups containing light atoms, corresponding to the stretching of chemical bonds and the deformation of interbond angles.⁵⁶² This form of spectroscopy offers a "fingerprint" or "signature" characteristic of the molecular constitution. If the sample is the surface of a sheet of paper then it is examined optically in reflectance by a technique known as Attenuated Total Reflectance (ATR), and with modern instrumentation the spectrum is acquired by a Fabry–Perot interferometer, and the resulting interferogram is analysed mathematically by subjecting it to a Fourier Transform (FT), so this infrared (IR) technique has come to acquire the grand abbreviated title of ATR–FTIR spectrometry.

Chemical bonds of a given order between specified atoms tend to vibrate with closely similar characteristic frequencies, referred to as *group frequencies*. More polar groups tend to produce stronger infrared absorption. In all spectra obtained from a paper surface, the group frequencies of the cellulose molecule will be present as background and are tabulated in Table 5.3 for reference.⁵⁶³

Frequency cm ⁻¹	Intensity & Character	Assignment
3330	ms vb	O-H str
2900	m b	C-H str
1640	w b	H-O-H def
1430	w sp	H-C-H def
1365	vw	C-C-H def
1330	vw	C-C-H def
1315	ms sp	C-C-H def
1280	vw	CH ₂ twist
1250	vw	C-O-H def
1200	w sp	C-O-H def
1160	m sp	C-C str
1110	m sp	C-O-C str
1060	m sp	CH-OH str
1030	vs sp	CH ₂ -OH str
1005	w sp	CH ₂ rock
985	w sp	CH ₂ rock
900	vw	C-O-C def
700	vw sh	
680	w sh	

Table 5.3 Characteristic infrared absorption bands of cellulose
all frequencies approximate ± 5 cm⁻¹

w = weak; m = medium; s = strong; v = very

b = broad; sp = sharp; sh = shoulder

str = bond stretching vibration; def = bond angle bending vibration

All descriptions of the assigned vibrational modes are approximate.

A typical spectrum of a cellulose fine-art paper is shown in Fig. 5.7.

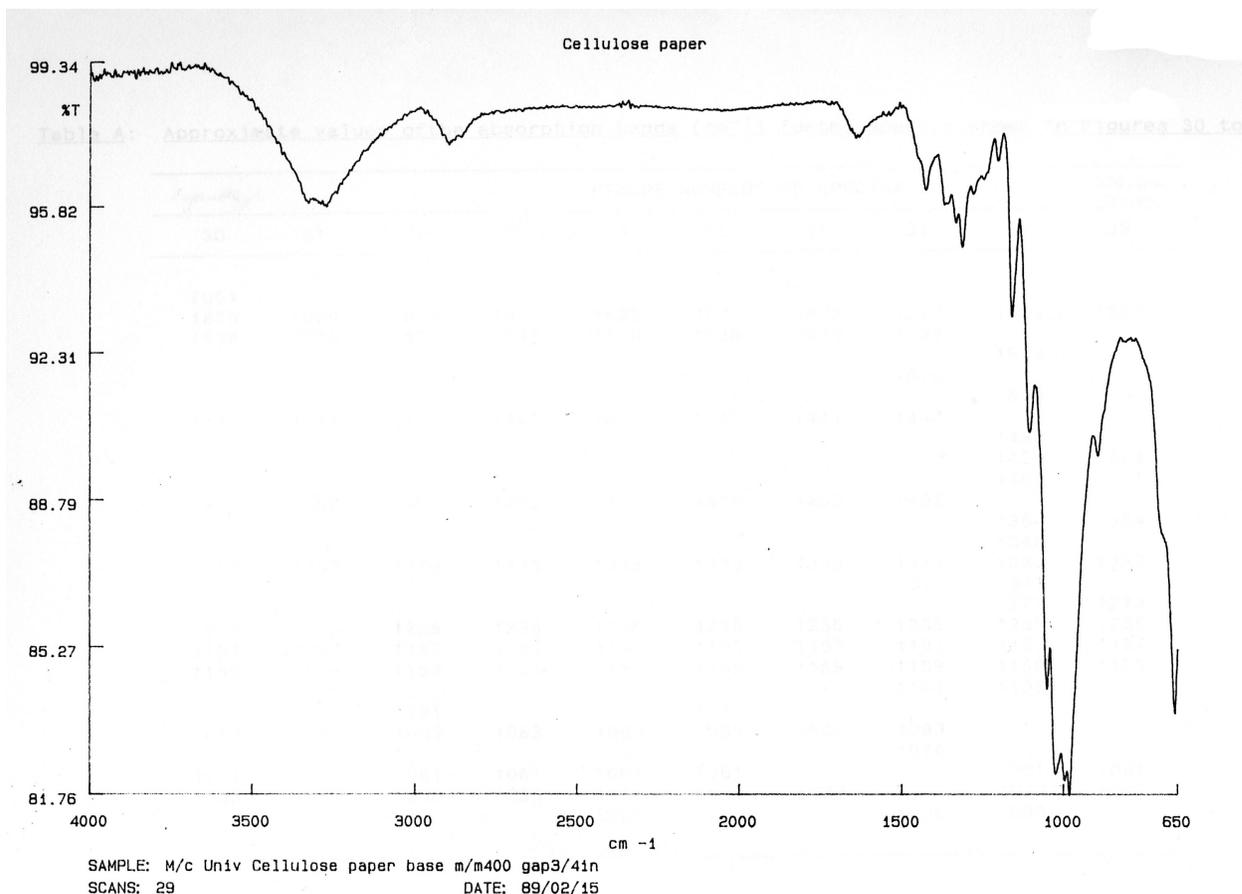


Fig. 5.7 IR spectrum of a typical cellulose paper (Fabriano 5)

The IR spectrum of Willis's KK Platinotype paper, coated but unexposed,⁵⁶⁴ also shows, in addition to the cellulose features, IR bands characteristic of the group frequencies of coordinated oxalate which correlate fairly well with those observed in ferric oxalate itself,⁵⁶⁵ see Table 5.4:

'KK' Pt paper	Fe ₂ (C ₂ O ₄) ₃	Intensity	Assignment
1715	1732	s sp	C=O str
1670	1666, 1614	vs	C=O str
1380	1384, 1348	s	C-C str + C-O str
1260	1264	m	C-O + O=C-O def
810	816	s	O-C-O def

Table 5.4 Infrared absorption bands of coordinated oxalate⁵⁶⁶

Like IR, Raman spectroscopy also records transitions due to molecular vibrations, but it does so by a process of light-scattering in the optical region rather than direct absorption in the infrared. The intensity of Raman lines is dependent on changes in the electronic polarizability – rather than the polarity – during vibration of the bonds, so it tends to favour those between heavy atoms.

The Raman spectrum of PtCl_4^{2-} with Pt–Cl stretching frequencies *ca.* 330, 312, and deformation at 171 cm^{-1} is well-known, but the original specimens of sensitized papers that have so far been investigated by this means show, in addition to the lines due to cellulose, features at 330 and 257 cm^{-1} .⁵⁶⁷

Coatings on photographic prints are also readily detected by ATR–FTIR spectrometry. Beeswax – essentially, myristyl palmitate – was a commonly used agent and gives bands characteristic of long chain aliphatic carboxylate esters.

5.7 Analysis and simulation of "Japine" paper

A concerted attack on the problem of identifying the nature of Japine papers, introduced in §1.15, was begun in 2012 by two teams of conservators and museum scientists, one from The Metropolitan Museum of Art, New York, which had secured an unopened tin of Willis's Japine paper, and shared its contents with the other team from the National Gallery, Washington; their preliminary findings were jointly published,⁵⁶⁸ followed by separate publications from each group of their detailed results.⁵⁶⁹

The findings can be summarised as follows: Japine prints and unexposed Japine paper were analysed for their organic constituents by Gas Chromatography–Mass Spectrometry (GCMS), with and without pyrolysis. It was found that they contain no proteins – *i.e.* colloidal binders such as albumen and gelatin are entirely absent. Carbohydrate analysis showed only the monosaccharide glucose, from the degradation of cellulose. There are no gums present. Resin analysis revealed the presence of abietic acid consistent with the papers being alum–rosin sized, as had previously been inferred.⁵⁷⁰ Microscopical examination of cross-sections showed a distinct compact surface layer physically resembling that seen in typical 'two-layer' prints such as albumen and silver gelatin prints, but without any of the baryta substrate seen in 'three-layer' prints. Prints on Japine paper are now described as belonging to the newly-defined print category: ***single-layer prints with modified surface***. The parchmentizing is more localised on the surface than it is in traditional 'vegetable parchment' papers, where it can extend throughout the thickness, but the carbohydrate analysis of the two kinds of paper is essentially the same.

Further experiments were successfully carried out at the NGA to simulate the partial parchmentization process, following Willis's comments in his Satista patent. Cranes 100% cotton paper, alum–rosin sized, was treated with 67% sulphuric acid for ten seconds at room temperature, followed by a brief wash, neutralization with ammonia and a water wash. It was found that the flatness and smoothness of the resulting surface layer was improved if the paper sheet was pre-humidified or even pre-wetted rather than dry. The resulting treated papers were successfully coated with platinum and palladium sensitizers and satisfactory test prints were made upon them.⁵⁷¹

5.8 Analysis and simulation of "Satista" paper

As previously indicated in §2.5, this flawed product, marketed in 1914, has given rise in recent years to conservation concerns over some important works in the photographic canon,⁵⁷² which provide the chief reason for including the process here for chemical consideration, although it is very little practised today. Satista was an uneasy hybrid of silver and platinum, according to Willis's patent of 1913, obtained as follows:

1) The paper was first coated with silver chloride; this was usually done in the manner of a salted paper print by 'double decomposition', but using a 5% solution of potassium chloride and 3% solution of silver nitrate, so the potassium chloride was in excess. As a consequence, the silver chloride formed would have very low light sensitivity, in contrast to salted paper printing, where the silver nitrate is in large excess (~12%), compared with the potassium chloride (~2%), to produce a sensitive variety of silver chloride.⁵⁷³ Willis also sometimes made an emulsion of silver chloride in gelatin and applied it by this means.

2) Next the coated paper was treated with his usual ferric oxalate solution (14%) in which a small quantity of potassium tetrachloroplatinate(II) was dissolved (0.2% to 1.2% instead of the 14% usually employed for platinotype).

3) After exposure, the paper was developed in strong potassium oxalate, cleared in acidified oxalate, then a 10% 'hypo' (sodium thiosulphate) bath to remove the residual silver chloride.

It is evident from these figures that the proportion of platinum in the image would have been small, its chief function is presumed to be catalysis of the reduction of the silver chloride by the ferrous oxalate photoproduct, *i.e.* it was essentially a platinum-catalysed modified kallitype process, see §2.4, because silver chloride alone is not easily reduced by ferrous oxalate, but silver nitrate could not be used here because, being soluble, it would react with potassium tetrachloroplatinate(II), precipitating silver tetrachloroplatinate, and possibly some silver chloride. The silver image of the kallitype process is notoriously vulnerable to residual iron(III) in the print, and it is not surprising that the Satista print has proved likewise.

Copy prints by Frederick Evans of woodcuts were mentioned in §1.13 and §2.5: one typical specimen of these prints was examined by Jacqueline Rees at the V&A in 1992 using X-ray fluorescence spectrometry,⁵⁷⁴ with the result she found the presence of both platinum and silver in the warm grey-brown image, which was perceptibly faded at the edges (Fig. 5.8). Rees argued that a print showing the presence of both metals in the image could have three possible origins regarding process:

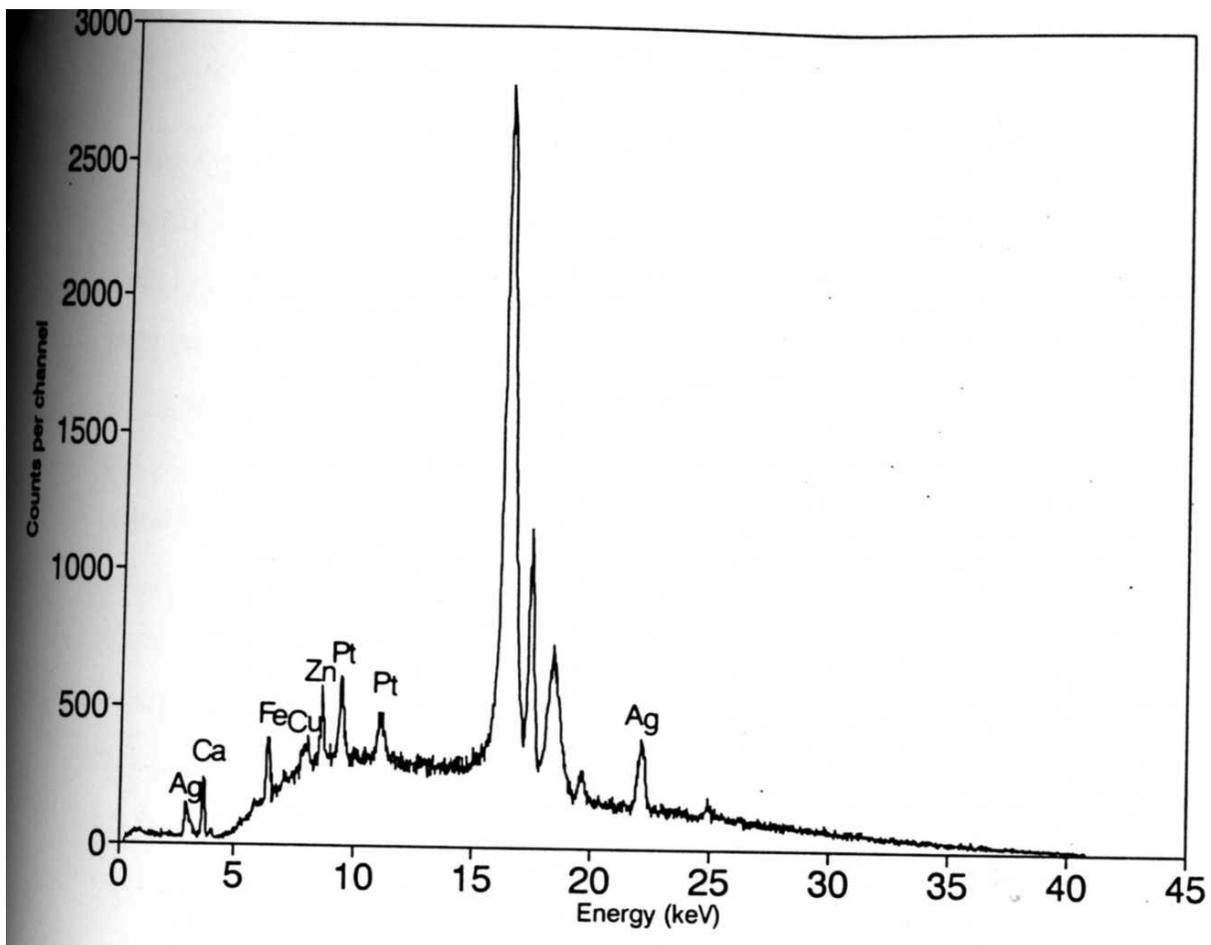
- a silver-toned or 'intensified' platinum print.
- a platinum-toned silver print such as 'Aristo-platino' paper.
- a print on Willis's Satista or Satoid papers.

Rees concluded that the fading, colour, and surface qualities of the print, such as the absence of an emulsion layer, suggested that, for this set of facsimiles, Evans had probably made use of Willis's Satista paper – which may have been hot-developed. No mercury was detected in the image.

Subsequent investigation of historic Satista prints has confirmed Rees's inference. In 2002 Lisa Barro examined twelve of Paul Strand's prints, made around 1916 (see §2.5), from the collection of The Metropolitan Museum of Art in New York.⁵⁷⁵ Her XRF spectra revealed that four were pure platinum prints, and in good condition, two were platinum–mercury prints, though it could not be inferred whether the mercury had been present in the original sensitizer – "sepia platinotype paper" – or was added to the developer during processing. The remaining six prints, which showed signs of deterioration and fading, contained platinum, silver and sulphur associated with the image substance – characteristics which are typical of "Satista" paper which had suffered some sulphiding, thus causing fading.⁵⁷⁶

In 2013, Stulik and Kaplan published their investigation of a Paul Strand Satista print from the collection of the J. Paul Getty Museum in Los Angeles.⁵⁷⁷ Their XRF spectrum is very similar to those of Rees (1993) and Barro (2002), but they also reported that their Satista prints had a surface gloss, like a thin varnish, which they identified as gelatin:

"The emulsion layer of Satista paper is usually very thin and difficult to identify using an ATR/FTIR spectrometer."



**Fig. 5.8 XRF Spectrum of suspected 'Satista' print
courtesy of Dr Jacqueline Rees, V&A Museum 1993**

5.9 Identification of toned platinotypes

"Sepia platinotypes" are generated either by including mercury salts in the sensitized coating, or by adding them to the developer (see §1.9, §6.7, §9.13 and §11.9). In both cases some mercury is deposited in the image, which has proved readily detectable by XRF in many historical specimens, as mentioned above for works by Stieglitz (§3.6),⁵⁷⁸ and Strand (§5.8),⁵⁷⁹ and in samples prepared for contemporary reference (§6).

Recently, Dusan Stulik and Tram Vo have recorded the XRF spectra of prints by Gertrude Käsebier from the collection of the J. Paul Getty Museum.⁵⁸⁰ 35 of those examined were platinum prints, and two turned out to be pure palladium prints – surprisingly, because these two were dated 1894 and 1896–9; so their early origin poses an interesting photohistorical question regarding the use of palladium. All the platinotypes, except one black specimen on Japanese paper, were also found to contain mercury, however only about 13 of these prints are described as "brown" in colour, 19 as "black" or "gray black", and two as "warm black". While this strongly suggests that the presence of mercury is a *necessary* condition to produce a brown platinum image, it also shows that it is not a *sufficient* condition, and it is not yet clear what additional factors must be present. The authors state that Käsebier used both hand-coated and manufactured platinum papers for her printing, but no assignment of her actual prints to these two categories was attempted. The authors remained under the misapprehension that:

"Commercial papers did exist for producing warm tones without the use of mercury; results indicated that Käsebier chose to do her own toning."

however, there is no reason why the observed mercury, in some cases, should not have come from the sensitizer of a commercial "sepia platinotype" paper (§1.9). Unfortunately, the results of this investigation have been even more confusingly misinterpreted by a blogger in the popular electronic media.⁵⁸¹

Stulik and Kaplan have used XRF to examine and identify several other examples of toned platinotypes in collections (for the chemistry of the various toning methods see §9.13).⁵⁸² These included a deep red-brown specimen which proved to be uranium-toned, and which also showed in its infrared spectrum the characteristic C–N bond-stretching frequency of the bound cyanide groups in the uranyl ferrocyanide pigment.

The presence of gold in pink, or purple-toned platinotypes has also been confirmed by these authors, in a gold-toned platinotype by Paul Strand (1928), suggesting that he used Dollond's toning process. The authors point out that an XRF instrument of quite high resolution (< 160 eV) is needed to resolve the overlapping L peaks of platinum and gold, adjacent in the Periodic Table.

5.10 Electron microscopy

It is only recently that state-of-the-art electron microscopes have been able to function at high magnification without coating the object with gold, and thus resolve the noble metal nanoparticles *in situ* for a platinum or palladium image on paper. Professor Patrick Ravines of Buffalo State College has been enabled by the equipment manufacturers FEI and JEOL Ltd., to apply their Variable

Pressure/Environmental Scanning Electron Microscopes (VP/E SEM) to platinum and palladium test prints, under magnifications up to 500,000 x.⁵⁸³ For an MW platinotype, single ellipsoidal Pt nanoparticles, of size 15–25 nm, were seen for the first time to be distributed evenly within the body of the surface cellulose fibres, 20–40 microns in diameter; see Fig. 5.9, in which the minute white specks layered within the fibre are the electron–dense nanoparticles of platinum. For a mixed Pt/Pd print agglomerations on the fibre surfaces were observed. The cellulose substrate was affected by the electron beam. Fibres could be cross–sectioned using an Ar⁺ plasma, carbon coated and imaged by secondary electron and back–scattered electrons.

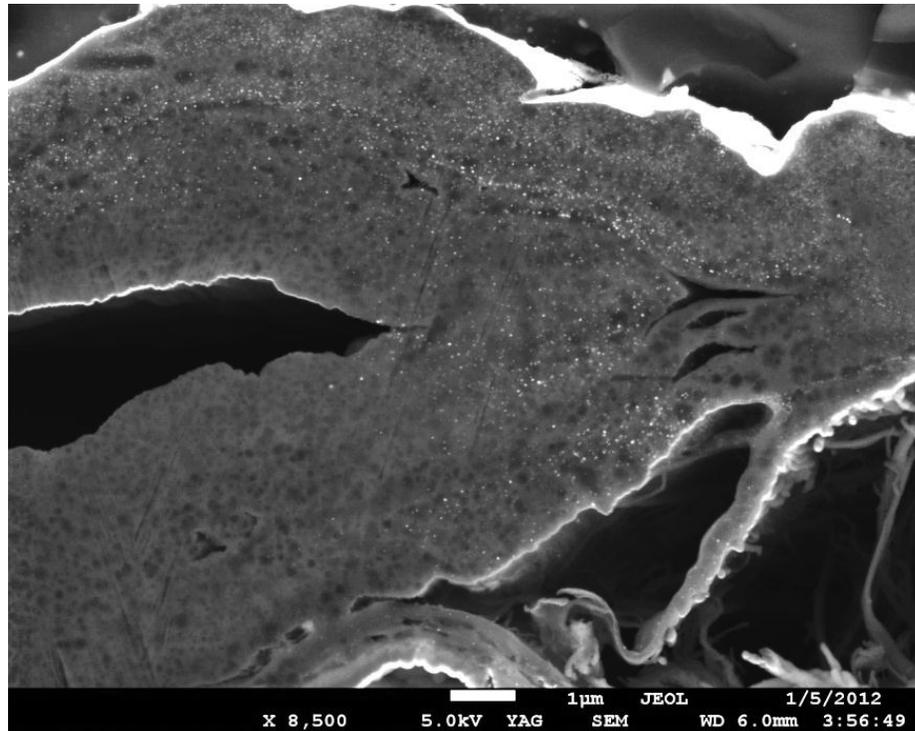


Fig. 5.9 Cross–section of a cellulose fibre in a Pt print 8500 x
Courtesy of Professor Patrick Ravines, Buffalo State College, 2012.

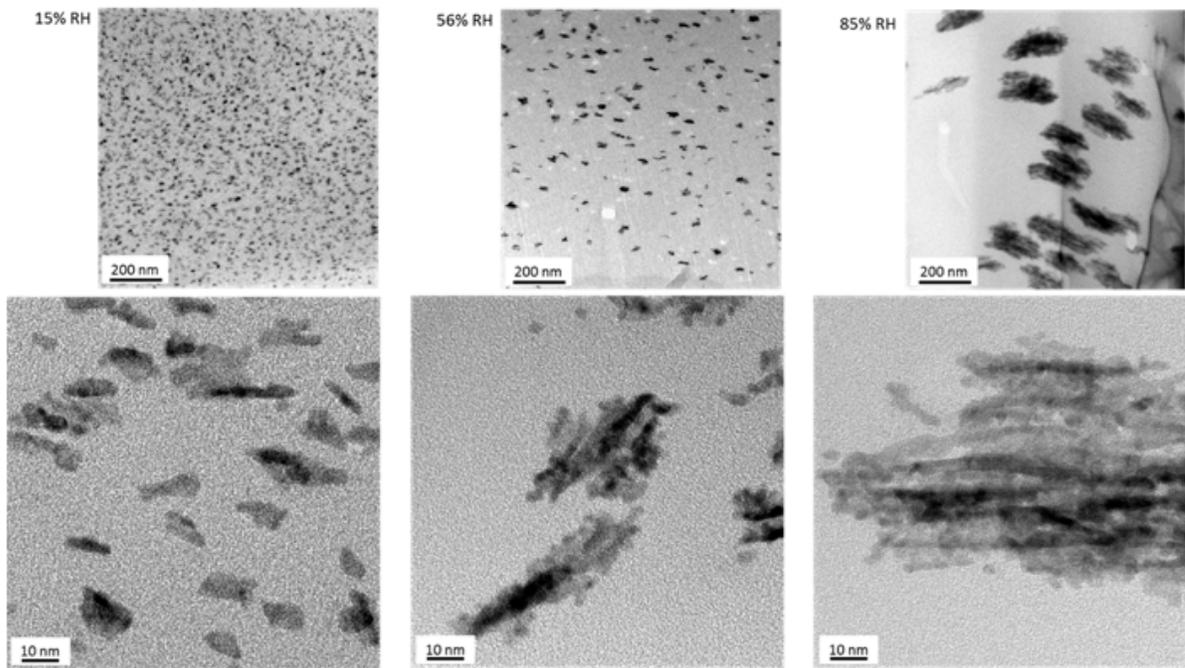


Fig. 5.10 Matthew Clarke's electron micrographs, showing the correlation of palladium particle size with relative humidity during printout.

6. Traditional Platinotype and Palladiotype

It is important to recognise that the content of this chapter is *not* being put forward as a working method for contemporary artist-practitioners wishing to print in platinum–palladium, although some still do persist with these obsolete materials and procedures. Better, updated methods now exist, using modern chemistry, which is more accessible and economic than the version described in this chapter, and has better prospects of endurance. A video comparing the two versions has been created by the National Gallery of Art.⁵⁸⁴ Full instructions for the modern printout process are given in chapter 7.

The purpose of this chapter is to describe how to fabricate platinum and palladium prints using scripted *historic* methods, in order to provide typical simulacra for investigation and testing – destructively, if necessary – by conservators and museum scientists.⁵ The materials and methods described here would have been available to, and used by, photographers at the time of original production over the period 1880–1940, and they have been derived from the historic literature. This chapter includes detailed information on the use of additives to the sensitizer, such as mercury and lead salts, which were of key importance to the evolution of the process but would not be generally recommended today for reasons of health and safety, and image permanence.

6.1 Expression of solution concentrations

Concentrations are expressed here as 'weight percent volume' (% *w/v*), which is equal to the weight in g (grams) of *solute* that is present in 100 cc (cubic centimeters or millilitres) of the made-up *solution*. Molarities are then easily calculated as $10C/FW$, where *C* is the concentration as % *w/v* and *FW* is the formula weight (or relative molecular mass) of the substance in grams. The instructions in modern formularies now tend to take the form:

'Dissolve X g of the solute in water (an approximate volume may be indicated as a guide) and make up the solution with water, with thorough mixing, to a final volume of V cc.'

It is obvious that this way of making up solutions can be accurately expressed by a concentration of C % *w/v* simply defined by:

$$C = 100X/V \text{ g}/100 \text{ cc}$$

This method is greatly to be preferred, especially if quantitative chemical reasoning is to be employed, and it is also the way of working that is natural for any trained chemist.

Contrariwise, most of the older formulations and recipes for making-up historic photographic preparations usually prescribe a procedure of the form:

⁵ *Etymological footnote 5: The word "simulacrum" (plural "simulacra") is preferred here to the more common "facsimile" because the latter denotes an exact copy of a picture, whereas the former only implies a "substitute", deriving from the verb "to simulate", meaning "to imitate the conditions of". It is curatorially undesirable to make facsimiles of images by Stieglitz etc!*

'Dissolve X parts (by weight) of the solute in V parts (by volume) of water (or other solvent).'

While it is easy to specify and carry out the making-up of a solution in this way, it also creates a quantitative uncertainty, because the dissolution of the solute in the solvent changes the total volume, so that the solution finally obtained no longer has a volume equal to V, but one that has been increased (usually) by an unspecified and unpredictable amount that depends on the quantity and individual chemical identity of the solute. Only for dilute solutions, say 1% or less, is it a reasonable approximation to assume that V remains unchanged, and that the concentration may therefore be taken as % w/v, once the units have been converted to g/100 cc. Unfortunately, if a solution is made up in this way it becomes impossible to relate its concentration accurately to the more useful, rational, and chemically significant units of C % w/v, unless further information – the density or specific gravity of the solution – is available.

In some formulae in this book, the working procedure has been simplified by pre-determining the precise volume of solvent (water) needed to give the desired final volume of solution, without the necessity of making up the volume.

6.2 Ferric oxalate

This substance is a chemists' nightmare: ferric oxalate is ill-characterised, evidently polymorphic, apparently uncrystallisable, and the molecular structure was previously unknown, until one polymeric form of the solid, $\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$, was determined in 2015 (see §11.2). The product, however, is notoriously variable, its composition and properties depending on the method of preparation, *i.e.* on the supplier. As a result, very few fine chemical houses list it in their catalogues, and on the rare occasions that they do, it is significant that the price of ferric oxalate is usually about 100 times that of ferrous oxalate! Sources even differ over the state of hydration of the substance and therefore its formula weight is uncertain and variable:

<i>Anhydrous ferric oxalate</i>	$\text{Fe}_2(\text{C}_2\text{O}_4)_3$	FW 375.76
<i>See reference in §11.2</i>	$\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$	FW 447.81
<i>CRC Handbook of Chemistry & Physics</i>	$\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 5\text{H}_2\text{O}$	FW 465.83
<i>Alfa Aesar 31116 and Aldrich 38,144-6</i>	$\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$	FW 483.84

Solid ferric oxalate is slow and difficult to dissolve in water, although the final solubility is high. The solution decomposes in a relatively short time, said by some to be 6–9 months in the dark, thus introducing uncertainties in practice due to its changes with time. It is significant that at least one well-respected platinum–palladium printer always makes up a fresh solution of ferric oxalate the night before every printing session.⁵⁸⁵ A consistent source of ferric oxalate is necessary for the historic practice of traditional iron-based alternative photography. For the present research the author has been currently using the Bostick & Sullivan product imported via Silverprint of London.⁵⁸⁶ Preparative methods for ferric oxalate are considered in Appendix V.2.

The present work employed a stock solution *ca.* 1.03 molar in Fe, obtained by dissolving 12.5 g of ferric oxalate hexahydrate ($\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$, FW 483.84) in exactly 44 cc of pure water, and filtering, which results in a final volume of 50 cc of a 25% *w/v* solution, which is the same as originally specified by the analysis of Pizzighelli and Hübl.⁵⁸⁷ Complete dissolution takes a lengthy period of constant, efficient stirring at room temperature. The present work employs this standard stock solution of 0.515 M ferric oxalate, which is nearly 2x Willis's stated concentration in his sensitizer, but which is effectively diluted 2x by the addition of an equal volume of the platinum or palladium solution, before application to the paper. This resembles most previously recommended practice, going back to Paul Anderson's re-publication (§2.11) in 1937 of the 19th century recipes of Pizzighelli and Hübl (1882), which were studied and adopted by most later practitioners (*e.g.* Irving Penn §4.1).⁵⁸⁸

In making up ferric oxalate solution, Willis remarked in his patents that he added sufficient oxalic acid to render his ferric oxalate "freely soluble". Subsequent practitioners have used various amounts, from 0 to 5 g, but usually in the region of 2 g, of oxalic acid, $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$, FW 126.07, per 100 cc of the usual strength solution, *ca.* 25% *w/v*. However, as explained in §10.5, this component may affect the degree of printout, so this variable was tested for its effect over the range 0–5% *w/v*. It was found to increase the extent of print-out very slightly, but to have little effect on the degree of reversal, which is more strongly dependent on other factors: R.H., paper, and developer. For practical purposes, it is proposed to adopt a standard of 2 g per 100 cc. (2% *w/v* in $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$, 0.16 M in excess oxalate.)

Instructions for Preparing Standard 25% w/v Ferric Oxalate Solution

To be carried out in dim (tungsten) lighting, then total darkness.

1. Weigh out 12.5 g of ferric oxalate into a 150–200 cc beaker.
2. Add 1.0 g of oxalic acid dihydrate.
3. Add exactly 44 cc of distilled water from a measuring cylinder.
This should suffice to make up a solution with a volume of 50 cc.
4. Stir constantly and efficiently at room temperature in the dark for about **20 hours** until the solid is completely dissolved to a clear dark olive-green solution.
A tiny residue or cloudiness does not matter. Use a magnetic follower (stir bar) almost as large as the diameter of the beaker for maximum efficiency of stirring. Do not heat. Clamp the beaker for safety. Cover with a Petri dish lid to minimise evaporation.
5. Check in the measuring cylinder that its volume is 50 cc.
Filter through a Whatman Grade 1 filter paper in a small conical funnel directly into a brown storage bottle.
Label & date it. Store in the dark.

6.3 Potassium tetrachloroplatinate

The platinum salt universally employed by Willis and all his successors from 1873 until 1986 was potassium tetrachloroplatinate(II) (K_2PtCl_4 , FW 415.11) *aka* potassium chloroplatinite. Unfortunately its precise solubility seems not to have been clearly defined nor documented in the literature. For instance the 'popular' recipe (*Cassell's Cyclopaedia*)⁵⁸⁹ has it that '1 part of K_2PtCl_4 dissolved in 6 parts of water' (ca. 15.6% w/v) is saturated, but Paul Anderson and others prescribe dissolving 1 part in 5 parts of water (ca. 18.5% w/v) for the platinotype sensitizer.⁵⁹⁰

It is possible that the solubility is somewhat time-dependent, due to a known aquation reaction of the dissolved anion, with a half-time of 2.4 hours (see §11.7). The value for the solubility of K_2PtCl_4 quoted in the *CRC Handbook of Chemistry and Physics*, and repeated in the entry for 'potassium tetrachloroplatinate' in *Wikipedia*, is certainly erroneous. The apparent solubility is not, ideally, high enough for the best results, which accounts for the use of 'double-coating' by some practitioners to achieve a higher maximum density. Neither has the solubility been precisely defined in terms of molarity: if 10 grams of K_2PtCl_4 (FW 415.11) are dissolved in 50 cc of water, the final volume of the resulting solution is not known exactly, but is probably ca. 54 cc, corresponding to a solution strength of ca. 18.5% w/v, or 0.45 M in Pt. The following preparation of the standard platinum solution follows historical practice, but should be regarded as tentative. Recent experiment suggests that the figures above are correct.

Instructions for Preparing Standard Platinum Solution

1. Weigh out 5 g of potassium tetrachloroplatinate(II) into a 150–200 cc glass beaker.
2. Add exactly 25 cc of distilled water from a measuring cylinder.
3. Warm gently to 40–50°C (104–122°F) and stir slowly until all the red crystals have dissolved.
This may take several hours. Keep beaker covered with a Petri dish lid. A tiny amount of residual yellow insoluble sludge may remain.
4. Filter the solution through a small (5–7 cm) Whatman Grade 1 filter paper in a small conical funnel directly into a brown storage bottle.
Label and date it. Allow it to "mature" for 24 hours before first use.

Solubility dictates that the potassium tetrachloroplatinate(II) standard solution is necessarily slightly more dilute (ca. 0.45 M) than the palladium solution (0.5 M) so when mixing it with the ferric oxalate solution the volume ratio should be: ferric oxalate : platinum = 0.9 : 1; however, if they are mixed 1 : 1, the small excess of iron is unlikely to make a very significant difference.

6.4 Health warning: platinum allergy

Tetrachloroplatinates(II) are listed as "Toxic by ingestion, irritating to eyes, and can cause dermatitis and skin sensitization. Can be allergenic, causing

symptoms of asthma.”⁵⁹¹ Contact with tetrachloroplatinate(II), and other chloro-complexes of platinum, is known to cause symptoms of asthma (wheezing, coughing, running of the nose, tightness of the chest, shortness of breath and cyanosis), and dermatitis – eczema and urticaria;⁵⁹² some allergic individuals may become particularly sensitized to these biologically-active chemicals. Appropriately, ‘platinum allergy’ was first observed in 1911 as an occupational disease of photographic factory workers handling platinotype paper. Since then, workers in the platinum chemicals industry have been carefully monitored, and there is an extensive medical literature on the subject.⁵⁹³ The symptoms disappear on removing the cause: if you develop this allergy, then platinum printing is not for you – but you could still use palladium, which is non-allergenic. Never touch the surface of platinum-sensitized paper or immerse ungloved fingers in the processing solutions. See §3.12. Dust inhalation presents the worst hazard: it is better not to store large amounts of dried sensitized paper. Platinum metal itself is not implicated in this – so take comfort that there is no risk in handling fully-processed platinotypes!

6.5 Agents for increasing contrast

The formulae for platinum printing sensitizers published by Pizzighelli and Hübl in 1882 (see §5.3) employed an elaborate system for adjusting the contrast of the paper by adding controlled amounts of potassium chlorate, KClO_3 to the sensitizer solution. This 'drop-counting' method using three solutions for the sensitizer was reiterated by Anderson and his successors in the USA, and has become standard practice today with many users, whose negatives presumably have insufficient density range for successful printing by the unmodified platinotype sensitizer which has a very long exposure scale, *ca.* 2.0 (see results in Fig. 11.3, §11.6). Willis makes no mention of contrast control in his patents or sensitizer formulae,⁵⁹⁴ but the camera negatives of his day had a much greater density range, in general, than modern materials. Potassium chlorate is a strong oxidising agent,⁵⁹⁵ and its effect is to reoxidise some of the iron(II) photoproduct, thereby making it unavailable for reducing platinum(II) and so truncating the exposure scale of the process, providing a more distinct tonal separation in the final image. It has been noted that the use of potassium chlorate can cause a deterioration in image quality and an increase in image graininess; moreover, the 'false sparkle' of lost gradation in the empty highlights is aesthetically unacceptable for the platinotype ethos, where subtly nuanced high values are generally regarded as a desirable characteristic.

An alternative mild oxidising agent that was also recommended in the 19th century to increase contrast in platinotype, was the addition to the sensitizer of sodium hexachloroplatinate(IV) Na_2PtCl_6 . It is still sold (at a very high price, of course) for this purpose today and is said to cause less image deterioration than potassium chlorate.⁵⁹⁶ There are differing opinions as to whether it also works with palladium; one authority even maintains that it works with palladium but not at all with platinum.⁵⁹⁷ It cannot be employed with any chemistry involving ammonium cations, in sensitizer or developer, because ammonium hexachloroplatinate(IV), $(\text{NH}_4)_2\text{PtCl}_6$, has a very low solubility and will crystallise out.⁵⁹⁸

To achieve "brilliant prints" by Palladiotype, Willis & Clements' instructions recommended the addition of a very small amount of the strong oxidising agent potassium dichromate, $K_2Cr_2O_7$, to the potassium oxalate developer bath. This was employed by Paul Strand and Ned Scott to enhance the printing of "flat" negatives,⁵⁹⁹ and is still favoured by some today.⁶⁰⁰ However, it should be noted that potassium dichromate reacts readily with oxalic acid, being reduced to oxalato–chromium(III) complexes,⁶⁰¹ so this additive will not be stable in an oxalate developer indefinitely, and will lose effectiveness, especially at low pH.

With the availability today of better controls for modern negative–making, especially by digital means, contrast–enhancing agents, such as chlorate, hexachloroplatinate(IV) or dichromate, become unnecessary when a correctly calibrated negative is made. In the present work, to avoid introducing yet another variable, the use of these undesirable image–degrading agents will be avoided; moreover, the present tests use standard photographic step tablets as the negative, which have a density range (*ca.* 3) that always exceeds the exposure scale of the process (usually no more than *ca.* 2.4), so that, provided adequate exposure is given, the full tonal scale, from maximum density D_{max} to paper base white, should always be obtainable in the test print without recourse to contrast enhancement. For pictorial purposes, it is strongly recommended that the negatives should be made correctly in the first place (see Appendix IV).

6.6 Sodium tetrachloropalladate

The 0.5 molar solution of this salt (0.5 M in Na_2PdCl_4) can be made up in two quite equivalent ways, the choice depending on economy and availability of chemicals. Either palladium dichloride may be dissolved in a hot solution of sodium chloride, or an identical solution may be prepared by dissolving solid sodium tetrachloropalladate(II) salt, which is usually supplied hydrated with approximately $3H_2O$, but sometimes anhydrous.

Instructions for preparing standard palladium solution

EITHER

1. Weigh out 2.92 g of sodium chloride (0.05 moles NaCl, FW 58.44) AR Grade, into a 100–150 cc glass beaker
Use heat–resistant (Pyrex or Corning) glass
2. Add 30 cc of distilled water, and heat to *ca.* 70°C; dissolve the solid.
3. Add 4.43 g of powdered palladium(II) chloride (0.025 moles $PdCl_2$ FW 177.31) in small portions with stirring until all is dissolved to give a dark orange–brown solution.
This may take ca. 10 minutes to one hour.
4. Make up the solution to a final volume of 50 cc and filter through a Whatman Grade 1 filter paper in a small conical funnel directly into a brown storage bottle.
Label and Date it.

OR

1. Weigh out **either** 8.7 g of sodium tetrachloropalladate(II) trihydrate (0.025 moles of $\text{Na}_2\text{PdCl}_4 \cdot 3\text{H}_2\text{O}$, FW 348.3) **or** 7.35 g of sodium tetrachloropalladate(II) anhydrous (0.025 moles of Na_2PdCl_4 , FW 294.19) into a 100–150 ml glass beaker:
Use heat-resistant (Pyrex or Corning) glass
2. Add 30 cc of distilled water; stir and warm to dissolve the solid.
3. Transfer the solution to a 50 cc measuring cylinder and make it up with distilled water to a final volume of 50 cc.
4. Filter the solution through a Whatman Grade 1 filter paper in a small conical funnel directly into a brown storage bottle.
Label and Date it.

The two solutions, of ferric oxalate and either potassium tetrachloroplatinate(II) or sodium tetrachloropalladate(II), are mixed in equal volumes shortly before coating (*i.e.* the same day) to make the sensitizer solution to be applied to the paper, which therefore has metal concentrations similar to those specified by Willis in his patent no. 1117 of 1880, and identical with those employed by most later practitioners in the 20th century.

6.7 Salts of mercury(II) and lead(II)

Pure platinum printing, using only the simple sensitizer of ferric oxalate and potassium tetrachloroplatinate(II), often yields a weak, fibrous or 'grainy' platinum image. The cause of this is the slowness of reduction of the platinum(II) complex to platinum metal by the iron(II) photoproduct, and consequently the exposed sensitizer chemicals being washed out of the paper by the wet processing before the image is fully formed. Moreover, the platinum redox chemistry may be inhibited by impurities or additives in the paper, such as gelatin, which can coordinate strongly to platinum(II) and further de-activate it. Willis found that certain substances, notably the salts of lead(II) and mercury(II), could hasten the response of the platinum chemistry, thus improving the image quality by smoothing out and intensifying the tones. Mercury(II) was used to make Willis's 'Sepia' papers (§1.9). We have evidence from his patents that William Willis commonly added lead(II) salts to his Platinotype formulations in order to obtain acceptable images in platinum, as follows:

Patent no. 2011 (1873) specifies coating the paper separately with a lead(II) nitrate solution of "40 grains per ounce", *i.e.* 9.12% *w/v* or 0.275 M in $\text{Pb}(\text{NO}_3)_2$ (FW 331.2), before applying the solutions of ferric oxalate and platinum.

Patent no. 2800 (1878) uses a sensitizer solution containing "2 grains of plumbic chloride per fluid ounce", *i.e.* 0.456% *w/v* or 0.0164 M in PbCl_2 (FW 278.1, which we now call 'plumbous chloride'). This patent also introduces the optional use of mercury(II) salts, which have an improving effect similar to lead, but also cause a colour shift – from neutral greys to sepia, and other shades of

brown. Mercuric chloride was recommended at a final concentration in the sensitizer of "4 grains per ounce", *i.e.* 0.912% *w/v* or 0.0336 M in HgCl₂ (FW 271.5).

Patent no. 1117 (1880) "dispenses with the lead salts... avoiding their use" but by 1887 Willis found himself obliged to return to using lead and/or mercury in later improvements.

Patent no. 1681 (1887) uses a ferric oxalate coating solution containing amounts of lead and/or mercury similar to the earlier Patent no. 2800, namely, 1 to 3 grains per fluid ounce: "I find the mercuric salt very useful where a warm tone or effect somewhat resembling that of sepia is desired."

Patent no. 16003 (1887) has Willis stating: "I now find, however, that, by ensuring the presence or contact of a salt of mercury or of lead with the image or picture at the time of its development, I obtain a better reducing action ..." and he again recommends the use of 1 or 2 grains of lead chloride or mercuric chloride per fluid ounce of sensitizer, or 5 grains of mercuric chloride per fluid ounce of the developer, *i.e.* 1.14% *w/v* or 0.042 M in HgCl₂.

Later formulations by others for the sepia platinotype prefer to use mercuric citrate,⁶⁰² at the level of 0.02 to 0.1 M in Hg final concentration, which was first proposed by Hübl in 1902 (see §1.9, §1.16) and is easily made from mercuric oxide and citric acid.⁶⁰³ It has the advantage of not requiring hot development.

The premature washing out of 'undeveloped' sensitizer image substance may be inhibited by increasing the viscosity of the developer with an inert water-miscible liquid such as glycerol, to diminish the rates of diffusion. This stratagem provides the basis for the "glycerine method" of local development, first described by Willis *ca.* 1893,⁶⁰⁴ and later taken up by Stieglitz and Keiley in their "glycerine development" procedure for Platinotype *ca.* 1900.⁶⁰⁵ It was often employed in conjunction with a mercury(II)-containing developer.

Although they were incorporated in the formulations for sepia Platinotypes, mercury and lead need *not* be introduced into the palladium sensitizer. The justification for this omission is that palladium has been found to be much less responsive than platinum to the effect of mercury as a toning agent – palladium images are already naturally brown – and mercury(II) tends to make them more neutral in colour, so there is little reason to employ mercury. Only if the analytical evidence demands it for the image quality, and if the presence of mercury is not simply adventitious (from used developer or cross contamination), should mercury be admitted into the sensitizer formulation; mercury introduces problems of toxicity and environmental disposal, so all precautions regarding residues and effluent waste must be taken.

6.8 Choice of papers

Willis did not disclose the source of paper rawstock for his commercial product, but as described in §5.2 it is believed originally to have been a "bespoke" Steinbach paper called "papier de Saxe", and latterly to have been BFK Rives No. 74 or 75. Willis recognised the importance of an appropriate sizing agent from an early stage, avoiding gelatin, which does indeed complex platinum(II) in aqueous solution and renders it less readily reducible to the metal (§5.2, 11.5).

To mimic the papers employed as platinotype rawstock ca. 1900 we adopted the following criteria:

- 100% cotton or linen cellulose. No lignins, which cause discoloration.
- A non-gelatin sizing agent, preferably alum-rosin, which is acidic, and which has now been confirmed analytically to be present in Willis's Platinotype papers, see §5.4.
- There must be no chalk additive as an alkaline buffer, which is almost universal in modern fine papers, but is destructive towards the iron chemistry, causing decomposition of the sensitizer, see §8.6.

Unfortunately, the second and third of these requirements run contrary to the changing trend in recent industrial papermaking practice, and current international standards (§8.6).

Tests for the present Project were begun initially using Arches Aquarelle – which is gelatin sized – but was found to be disadvantageous, due to some crystallization occurring on the surface, and a slow response. A surfactant (Tween 20) did not fully cure this.

Some of Cranes' papers have been found suitable in the past: Kid Finish Ecru White was used by Gottlieb in 1993, and Kid Finish AS8111 was recommended by Crawford. The author found that Cranes Crest Parchment and Cranes Cover tested well. These papers seem no longer to be available, but a stock of Cranes '100% Cotton' paper has been unearthed, which is serving well as a test substrate. Neenah Papers of Wisconsin now still make 100% cotton alum-rosin sized papers, but samples so far have not been of an appropriate colour.

A possible replacement paper recently launched on the 'alternative photographic process' market is Weston Diploma Parchment, from Butler-Dearden Company, which is alum-rosin sized, unbuffered, and is currently being tested. This paper seems to suffer from the disadvantages that (i) it is very absorbent, and inadequately sized, (ii) the yellow dye or pigment incorporated to impart the paper's "creamy" colour is not sufficiently fast and is washed out from the palladiotype sensitized region in the wet processing, (iii) the paper is not retentive of iron(III) salts – possibly due to the absorption of Al^{3+} ions at the cellulose sites that would otherwise bind Fe^{3+} , so it tends not to 'stain' easily (this is of course, an advantage for the printer, actually, but not the researcher of staining!), (iv) under oxalate development, but less markedly so under citrate, the sensitized area randomly generates small black specks – presumably due to some particulate, reducing-agent impurity in the paper.

It may also be possible to seek historical paper specimens through the British Association of Paper Historians. Of other contemporary papers, Arches Platine and Atlantis Silversafe Photostore both work well, serving as matt surfaced papers, but they use a modern alkyl ketene dimer (AKD) internal sizing agent, "Aquapel", rather than alum-rosin, so are not typical of 19th Century papers. Investigations are underway to discover which paper can best be used to simulate the "Japine" surface supplied by Willis and used with approval by Stieglitz; a partially parchmented paper will be required or possibly a *simili Japon* paper. Preliminary results with Cranes 100% cotton paper that has been

partially parchmented by treatment with concentrated sulphuric acid show that it performs well with platinum and palladium sensitizers.⁶⁰⁶

6.9 Silica and aluminosilicates in papers

There is some evidence from the EDX spectrum that Willis's papers may have contained a clay or aluminosilicate, such as kaolinite, which is commonly added as a filler to many commercial papers for economic reasons connected with the rate of drying, and to increase the opacity and surface smoothness. Such an additive to the paper may also improve the absorptivity towards aqueous sensitizer solutions. It appears that colloidal silica was added to the formulation of some of the Huey Company commercial cyanotype papers in the mid-20th century to improve sharpness and image density.

Recently the use of fumed silica powder, scrubbed dry into the cellulose paper sheet before coating, has been advocated as a means of improving the D_{\max} of siderotype images on papers whose performance is otherwise deficient.⁶⁰⁷ The present author is inclined to regard this procedure as a violation of the artistic principle of "truth to materials", so it has not been tested in the present investigation, and inferior papers that are said to benefit from it are simply avoided. Moreover, the inhalation of nanoparticle silica can lead to a respiratory disease known as 'pneumonoultramicroscopic silicovolcanoconiosis' so appropriate verbal protection should be adopted when working with it.

There is evidence that the use of fumed silica may retain more sensitizer in the surface layer and thus can enhance the D_{\max} of palladium-platinum prints of the traditional kind,⁶⁰⁸ if this parameter is of compelling importance to the practitioner, then the advice is to use a fumed silica of the hydrophilic variety, and preferably as a stabilized aqueous dispersion, such as Ludox, rather than as dry powder, although the alkalinity of such suspensions may cause problems with Fe(III) retention in the image (§9).

6.10 Coating procedure

Specific coating weights and volumes of sensitizer per unit area of paper can be inferred from Willis's patent specifications as in §5.1, and will be simulated as accurately as possible. Specific sensitizer coating volumes, per unit area, for typical papers are controlled by the absorptivity of the paper and the nature of its sizing, and usually fall in the region of 24–36 cm³/m² giving coating weights of platinum or palladium of 6–9 millimol/m², which accords with the upper value (6.72) for Willis's stated coating weights for platinum, calculated from his patent specifications (§5.1). The sensitizer is only mixed when needed for coating the same day, and its total volume obviously depends on the number and size of sheets to be coated. As a rough guide for Cranes 100% cotton paper, allow 1.4 cm³ for each area of 21x26 cm (8"x10"). Thus a total of 100 cm³ of sensitizer suffices to coat ~70 sheets of 8.5"x11". Other papers may, however, have different absorptivity. See Cobb Test §8.2.

Since Willis's factory-made paper was mechanically coated under "hygienic conditions",⁶⁰⁹ the use of a glass rod, rather than a brush, for hand-coating the present tests seems more appropriate and controllable. Papers naturally differ in their absorptivity of the sensitizer; sufficient is used to ensure that the

surface fibres are saturated by the coating process; four or five 'passes' of the coating rod, taking about half a minute in total, appear to be adequate. Further description of the coating rods etc., are on the author's webpages,⁶¹⁰ whence a brief video can also be downloaded.⁶¹¹ The detailed sequence of instructions for the coating method, which is carried out under dim tungsten illumination, is described in detail in §7.16.

6.11 *Drying and humidity control*

Ambient relative humidity (usually RH *ca.* 55% ± 5% in MW's studio) is used for many tests, and at least one hour is allowed for the paper to come to equilibrium with the atmosphere. This condition would be typical of 'hand-coated' practice, where the sensitized paper is printed the same day. However, sensitized platinotype paper does not last for longer periods unless it is well-dried in order to inhibit the decomposition reactions. To achieve an economic 'shelf-life', complete desiccation was a commercial imperative for the manufacturers and purveyors of platinotype papers, like Willis, who marketed the product sealed in tins containing the desiccant, anhydrous calcium chloride.

To simulate the dry conditions of the commercial paper, the freshly-coated paper is 'rested' for about 10 minutes to allow absorption of the sensitizer by the cellulose fibres, then heat dried in an air stream at 45°C for 10 minutes, then stored in a calcium chloride (granular anhydrous CaCl₂) desiccant chamber at *ca.* 9–27% RH. Other controlled RH environments can also be used, by employing saturated solutions of various salts (§7.18).

At least one hour is allowed for the equilibration. The process of drying and rehumidification is found to be reversible, but there is a hysteresis in the response to water, as shown by the isotherms (Fig. 8.3). The ambient and container RH values and temperatures are monitored with thermohygrometers, a convenient model having a remote probe.

6.12 *Test target images*

The author's test target 'A' consists of multiple identical step tablets (8 x Stouffer T3110, each having 31 steps in density increments of 0.1), allowing subsequent division of the sheet, differential processing and semi-quantitative comparisons, see Fig. 6.1. The step tablets are mounted on glass in a hinged-back contact printing frame. The sensitized paper should be backed with a felt blanket, preferably conservation grade, or other thick porous sheet, in order to take up the evolved carbon dioxide gas – as explained in §7.20.

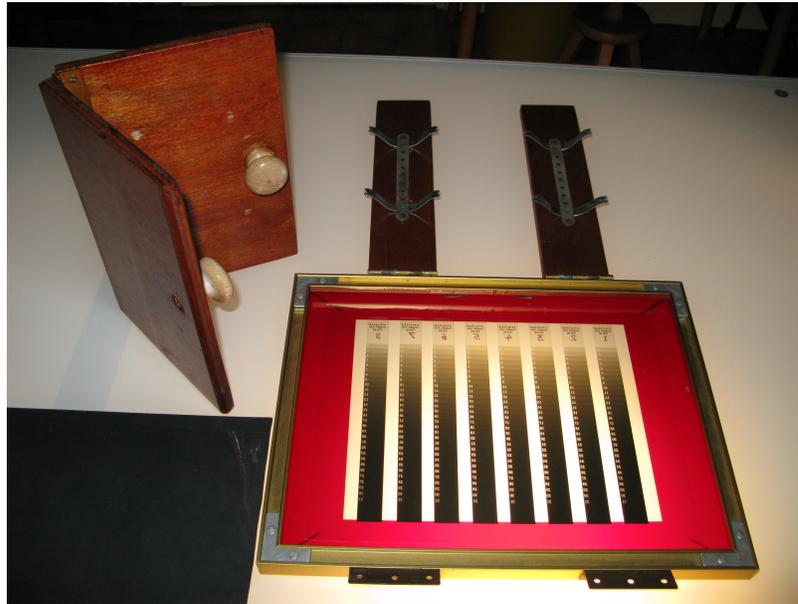


Fig. 6.1 Test target 'A' of 8 step tablets for contact printing.

Care is taken to include regions of paper, masked from irradiation with rubylith, to provide information on residual substances in non-exposed but coated areas, where the stain will be most evident. For generating sample images to test treatments for the removal of the yellow stain, a different test target 'S' was prepared, consisting of a 10"x8" Stouffer step tablet TLF 2115 masked by seven strips of rubylith tape to provide large areas of coated but unexposed paper, adjacent to step images to check for any loss of metal density resulting from the treatment.

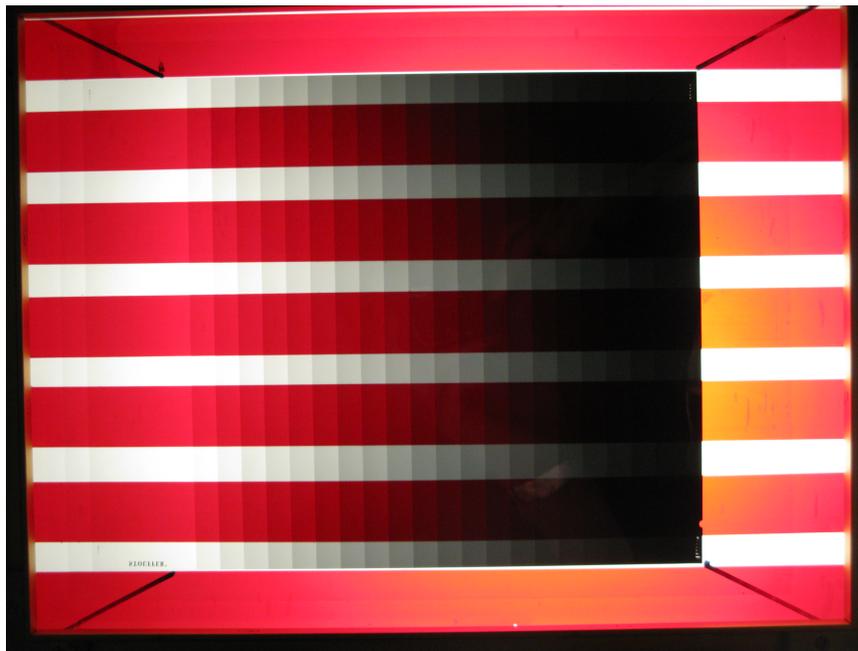


Fig. 6.2 Test target 'S' for printing stained images for treatment

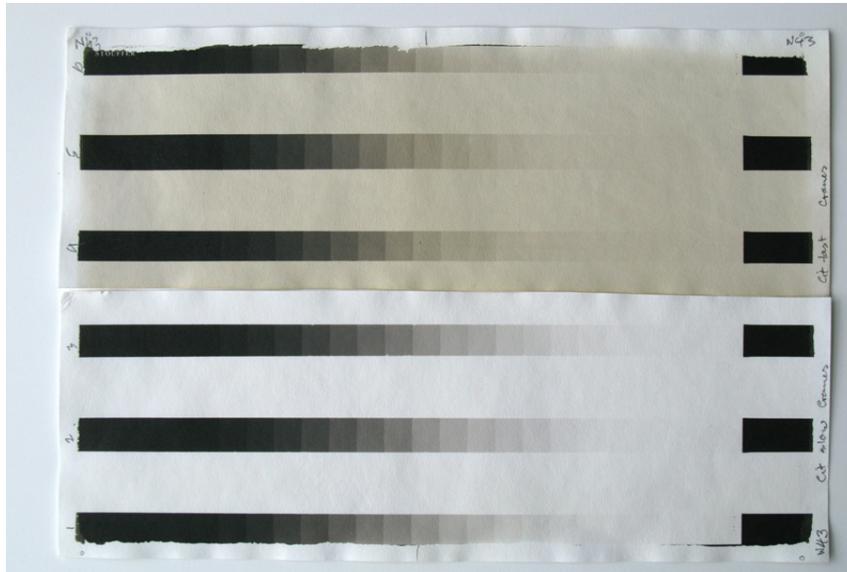


Fig. 6.3 Test print showing deliberately stained portion

Because there is no Callier Effect in contact printing, the logarithmic exposure scale for a given result can be assessed from the optical density range between the last step printing maximum black and the first step printing paper white, in ascending order of step number. For the T3110 tablet this is conveniently given approximately by:

Exposure Scale = Density range = (First White Step No. - Last Black Step No.)/10

6.13 Ultraviolet light source

Sunlight is too variable and uncertain as a light source for a controlled investigation of printing – especially in the UK. The current work employs instead a domestic facial tanning unit made by the Philips Company, comprising 6 UVA actinic/09 fluorescent tubes, 400 mm long, having a power of 20 watts each: a total of 120 W. The emissivity of these tubes peaks at a wavelength around 365 nm, which has been calculated to be the optimum wavelength for the siderotype processes, see §12.5.

Before each test exposure, it is 'run up' for about 5 minutes to ensure that the tubes are warm enough to have reached a steady light output, which takes about 3 minutes.

The printing light source used by Stieglitz and most of his contemporaries was – presumably – the sun. The Cleo UVA unit may produce significantly different results from that traditional source in two respects: by causing less heating to the object, and by causing less sharp acutance in the images if a plastic film is interposed between negative and paper (see §7.19) to protect the step tablets. The unit is shown in Fig. 6.4.



Fig. 6.4 Philips 'Cleo' UVA facial solarium.

6.14 Exposure determination

This was achieved by test stripping successive steptables in intervals of 1/3rd stop and looking for a suitable distribution of tones across the scale, ensuring a maximum density (D_{max}) in Steps 1 & 2 at least. Standard exposure times of 5 or 10 minutes were settled on for all the tests with the Cleo lightsource, for both platinum and palladium, for ease of comparability.

6.15 Platinotype processing

As Platinotype developer, Willis recommended neutral potassium oxalate, 120 to 130 grains per fluid ounce (27–30% w/v). Later practice was little different, recommending saturated (~32% w/v) potassium oxalate, $K_2C_2O_4 \cdot H_2O$, (aka dipotassium ethanedioate monohydrate FW 184.24). Before 1892, the developer solution was used hot to bring about more rapid chemical reduction. A standard developer 28% w/v in potassium oxalate monohydrate was used in the present work, at room temperature. Texts say the developer should be neutral or just slightly acid, to counter any accumulated alkali from water or paper, as the developer was reused. If much more than a trace of acid is present, it is said to inhibit the formation of platinum. (Crawford) Some recipes have 0.1% added oxalic acid or less. It may be noted that some modern practitioners of the traditional process recommend the addition of ~2% excess oxalic acid to the developer – presumably to lower the pH <6 and inhibit the hydrolysis of iron(III) and avoid staining.⁶¹² As a modification, said to generate cooler, bluish tones, the Platinotype Company also marketed its proprietary "Special D Salts" Platinotype developer, which we now know contained the following substances in the approximate proportions (% w/v) indicated:

Potassium oxalate monohydrate	85 %
Potassium dihydrogen phosphate	12 %
Oxalic acid dihydrate	3 %

The mixed salts were dissolved in sufficient water to make the working strength of only 8.6% *w/v* for the developer for black papers at room temperature, and of 10.3% *w/v* for the Sepia Japine papers at 70–80°C, although some workers used more concentrated developer.

Black Platinotypes were then directly cleared in three successive baths of hydrochloric acid, the concentrated acid (36% *w/w* HCl *ca.* 12 M) diluted 1:60 (0.2 M, pH<1) for about 10 minutes each. For Sepia Platinotypes a more dilute acid of half that strength was recommended. These clearing procedures were intended to remove the residual iron salts from the print, but were not always successful and some workers employed much longer clearing times. Finally the print was washed in water for about 30 minutes.

6.16 Palladiotype processing

Here the details for Palladiotype are unambiguous and straightforward from Willis & Clements instructions published in the USA,⁶¹³ which agree with the recipes published in the UK by the Platinotype Company.⁶¹⁴ Obsolete units of weight and volume have been converted here to give all concentrations in weight percent volume (% *w/v*) *i.e.* the number of grams of solute that are present in 100 cubic centimeters of the made-up solution.

Developer: Trisodium citrate dihydrate $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ (FW 294.10), 20% *w/v* + citric acid, $\text{C}_6\text{H}_8\text{O}_7$ (FW 192.12), 2.2% *w/v*. Treat for as long as necessary to develop the image: 4–5 minutes.

Clearing bath: Trisodium citrate dihydrate 20% *w/v* + citric acid 9% *w/v*. This stock solution is diluted 8x for use, to 2.5 % citrate + 1.1% citric acid, and 3 sequential baths are employed for at least 10 minutes each. Final wash is given in running water for 30 minutes.

More dilute solutions (*ca.* 4x) were recommended for the Sepia Vellum Palladiotype paper.

However, the problem, as already stated in §2.7, is that this procedure, recommended by the manufacturer and the distributor, seems not to have been generally adopted in the USA. According to the evidence from Paul L. Anderson: to develop their Palladiotypes many American workers chose simply to employ their pre-existing, used Platinotype developer solutions, consisting of (nearly) saturated potassium oxalate – plus all their accumulated metal salt residues. However the Palladiotypes, according to Anderson, must be cleared in 1:200 hydrochloric acid, not the 1:60 acid used for platinum, which otherwise dissolves palladium and bleaches the image partially. This was confirmed by McCabe and by Gottlieb in 1993.⁶¹⁵

6.17 Processing variations

All current tests of Palladiotype by MW are being carried out with both citrate and oxalate developers, for comparison. They show evidence that the oxalate developer can reduce the Pd(II) to some extent, thereby causing a brownish grey fogging of the highlights by palladium metal, quite distinct from the yellow stain of iron. Oxalate also produces a warmer colour and higher speed. Clearing is in 1:200 hydrochloric acid or dilute acidified citrate, according to the two 'traditions' of Palladiotype processing – US and UK. The hydrochloric acid bath

will tend to etch away the 'fog' of palladium in the high values, especially if 1:60 dilution is used, so the two procedural faults in US processing tend to be self-cancelling. The citrate development bath recommended by Willis leaves clear highlights, see Fig. 6.7.

Some samples will be deliberately treated with very short clearing times to simulate Alfred Stieglitz's 'impatience' as evidenced in §3.2. The total 'wet process time' is shortened from *ca.* one hour to 5 or 10 minutes, by immersing the print for only 1 or 2 minutes in the developer and each of the clearing baths, and washing for only 2 or 4 minutes in water. If coated paper is humidified before exposure by placing it in an environment of 75–80% RH for 4 to 24 hours, the staining will be further exacerbated. This intended generation of yellow stains can be investigated by artificial ageing in the NGA laboratories, followed by instrumental analysis: colour measurement, and X-ray fluorescence spectrometry of D_{\max} , D_{\min} , and the paper base, coated but unexposed, and uncoated, with a view to monitoring the iron and palladium contents.

6.18 Partial reversal of tonality

This is a conspicuous feature of some Stieglitz Palladiotypes as recounted in §3.7, so the conditions for promoting this phenomenon will be explored on various papers. Preliminary tests by MW, see Figs. 6.5 and 6.6, suggest that the principal factors promoting the reversal phenomenon are:

- a) Low relative humidity: $RH < 30\%$ for the dried, sensitized coat on printing.
- b) Oxalate developer is slightly more effective than citrate, but tends to cause fogging in palladium.
- c) The nature of the paper – possibly favoured by lower absorptivity.
- d) The extent of partial printout corresponds with the point of reversal.
- e) A contrasty negative ($\Delta D > 2.4$) allowing heavy exposure of shadows.
- f) Excess oxalate ion in the sensitizer might be expected to influence the degree of print-out and therefore the "reversal" phenomenon. With 'pure' ferric oxalate sensitizer under dry conditions there is very little printout at all, because the photoproduct, ferrous oxalate, is insoluble. The addition of some oxalic acid to the sensitizer, which is customary but not essential, appears to produce a little more printout, presumably due to the formation of the ferrioxalate anion, $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ (see §10.5) which remains soluble on photodecomposition and can migrate sufficiently before development to find the reactive noble metal salt and reduce it. The customary addition of 2% oxalic acid would cause about 10% of the ferric oxalate sensitizer to be converted into the ferrioxalate anion.

"Reversal" appears to occur much more frequently with the more reactive palladium than with platinum, and it may depend on a slight partial printout to mask the shadow tones from further exposure; in consequence there appears to be an optimum concentration of excess oxalic acid to produce the effect, which can be found experimentally to be in the region of 2% w/v. All these variables will be tested in the attempt to optimise the effect. Specimens will also be subjected to accelerated ageing conditions as described in §3.7⁶¹⁶

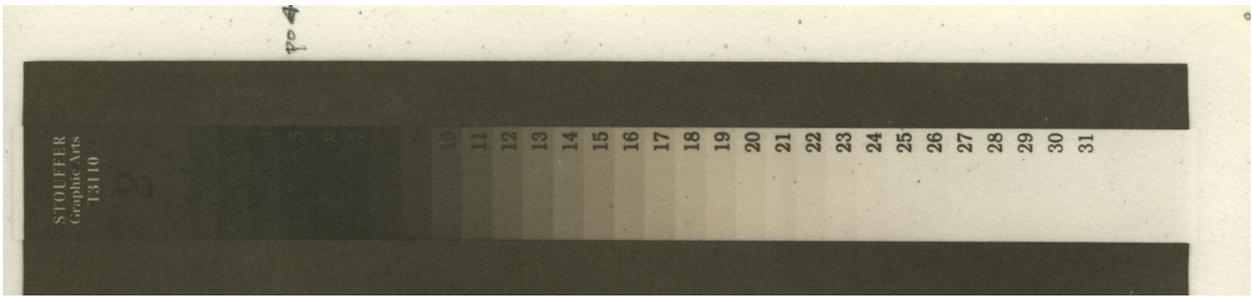


Fig. 6.5 Dry Pd print on Weston Diploma at RH=27% showing reversal

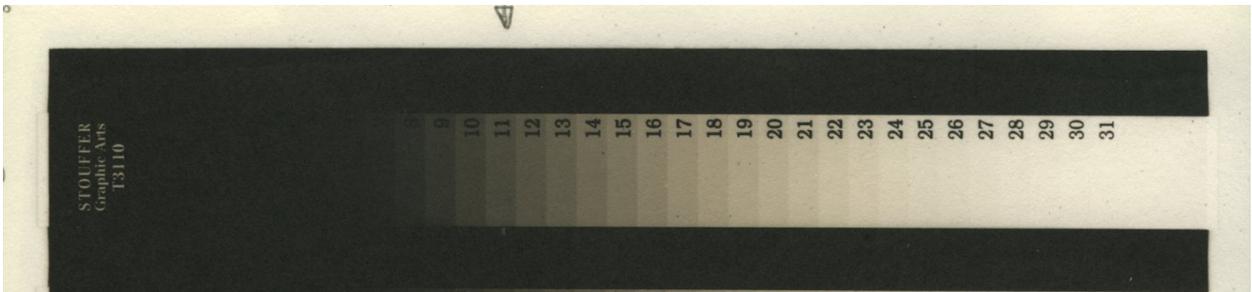


Fig. 6.6 Humid Pd print on Weston Diploma at RH=67%, otherwise identical

“Reversal” is not seen to occur with the modern printout process (§7), even using pure palladium, because the image build-up is relatively slow during the exposure, rather than sudden at the moment of development. It is a principle of physical chemistry (the von Weimarn coefficient) that faster reactions, giving greater degrees of supersaturation, tend to produce a smaller particle size in the precipitate (§11.4) with a consequent warmer colour.

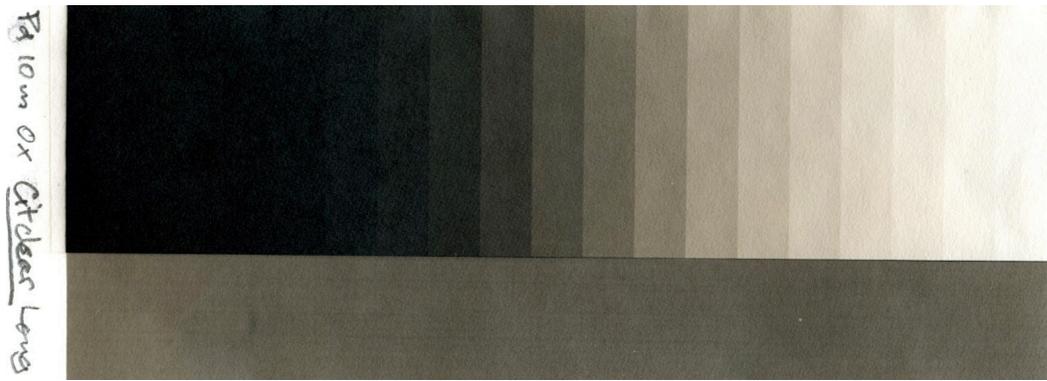


Fig. 6.7a Palladium developed in oxalate, cleared in citrate

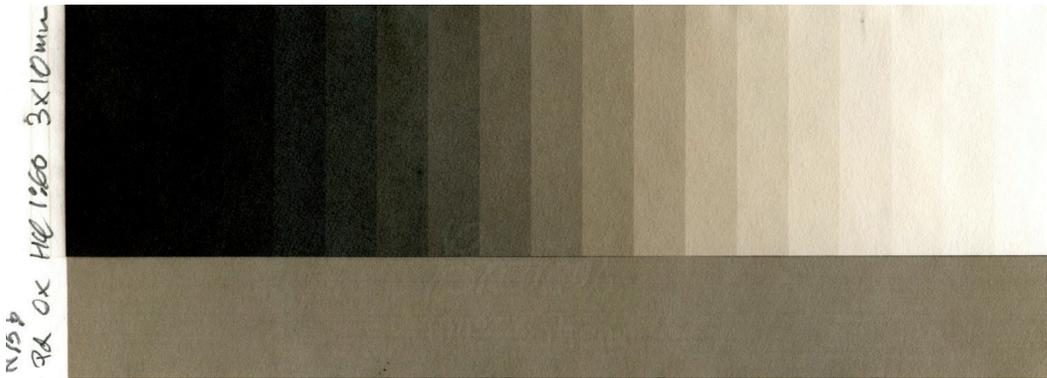


Fig. 6.7b Palladium developed in oxalate, cleared in 1:200 HCl

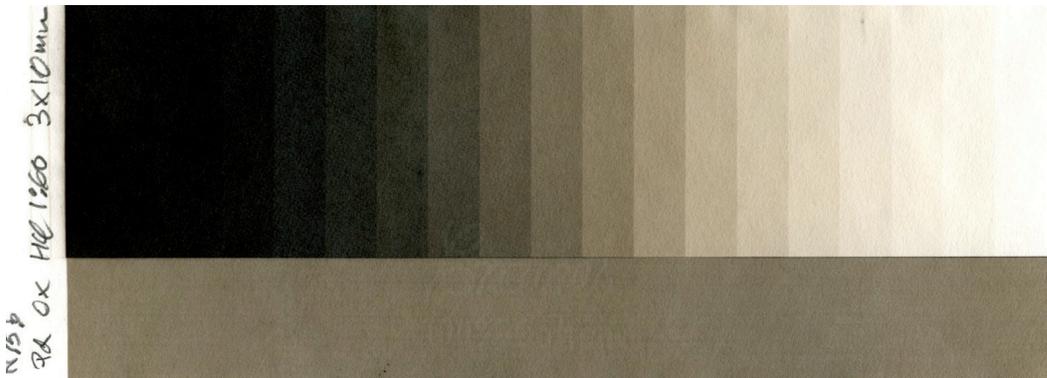


Fig. 6.7c Palladium developed in oxalate, cleared in 1:60 HCl

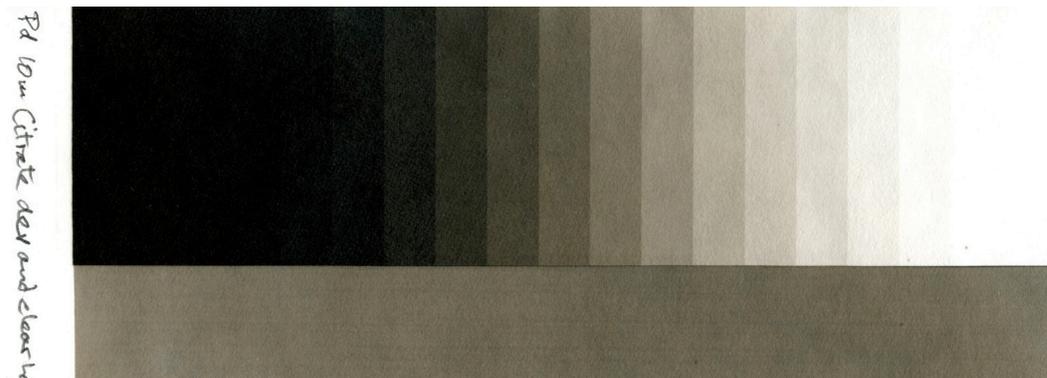


Fig. 6.7d Palladium developed in citrate, cleared in citrate

7. Modern Printout Platino–Palladiotype

In recent years platinum–palladium printing has regained its rightful place at the summit of alternative photographic practice; it is renowned for the subtly nuanced tonal qualities of its images, formed by permanent noble metals in matte–surfaced artists’ paper. Willis’s traditional Platinotype and Palladiotype (§6) are development processes, and capable of beautiful results – in skilled hands – but they suffer from some chemical inconsistency. This chapter is intended as a complete, self–contained instruction manual for the Malde–Ware printout method, which employs a better–behaved iron sensitizer, similar to that used in the print–out platinum process due to Pizzighelli in 1887 (see §1.16, §5.3, §11.2). A technical comparison with the earlier development process shows the advantages of this modern print–out version in economy, accessible chemistry, ease of exposure, control of image colour and contrast.⁶¹⁷ With the procedures described in this chapter, platinum or palladium may be used individually, or mixed in any proportion, offering a choice of the image hue anywhere between neutral grey–black and rich sepia, without further toning agents. A controlled degree of humidity is allowed in the sensitized paper, which promotes the formation of a print–out platinum–palladium image during the exposure, requiring little or no development. A carefully–devised clearing sequence ensures that all residual iron is removed from the paper.⁶¹⁸

7.1 Working environment

Your work–surface for preparing sensitized paper should be clean, flat, smooth, dry, level, and at a suitable ergonomic height: plate glass is recommended. You will also need a large wet–processing area, preferably a sink, to hold four photographic dishes of an appropriate size, together with a means for washing your prints in running water, and an indoor drying facility. In the interests of consistent results, it is desirable to maintain a steady temperature in the work environment, between 18° and 24°C (64° and 75°F), and preferably around 20°C (68°F). However, it is not essential to install air–conditioning for the entire work–space, because the relative humidity (RH) of the sensitized paper can be controlled locally by placing it in hydration boxes of known RH, as will be described below. The low sensitivity to light of siderotype papers has a practical benefit: you do not need to work in a blacked–out photographic darkroom, equipped with safe–lighting. Ordinary curtains or blinds should eliminate daylight sufficiently, and for preference the working area should be illuminated by an old–fashioned domestic light–bulb (incandescent tungsten): a rating of 40 watts, distant two meters or more from the sensitive materials, is safe for the working time periods normally involved. A light switch with dimmer control may also be found useful. Avoid using light fixtures with fluorescent tubes or lamps; most types of these have a significant output of ultra–violet light which may cause fogging of the sensitized paper in time. It is useful to maintain a completely dark enclosure somewhere in your work area, such as a cupboard or drawer, where sensitized papers can be kept for some hours or more while drying on racks or lines; it should be possible for the air to circulate freely through this enclosure, to avoid any build–up of humidity.

7.2 Sensitizer chemicals

Purity: General Purpose Reagent (GPR) grade *ca.* 98% is adequate.

These quantities will suffice to make *ca.* 60 10x8 in. Pt:Pd=1:1 prints

Substance, Formula & MSDS	Quantity
Ammonium iron(III) oxalate (NH ₄) ₃ [Fe(C ₂ O ₄) ₃].3H ₂ O <i>aka</i> ferric ammonium oxalate; ammonium ferrioxalate	30 g
Ammonium tetrachloroplatinate(II) (NH ₄) ₂ [PtCl ₄] <i>aka</i> ammonium chloroplatinite http://www.alfa.com/content/msds/english/11046.pdf	5 g
EITHER	
Ammonium tetrachloropalladate(II) (NH ₄) ₂ [PdCl ₄] <i>aka</i> ammonium chloropalladite http://www.alfa.com/content/msds/english/11882.pdf	5 g
OR	
Palladium(II) chloride PdCl ₂ <i>aka</i> palladium dichloride plus	3 g
Ammonium chloride NH ₄ Cl	1.8 g
Water, purified , H ₂ O (distilled, de-ionised, pharmaceutical, etc)	100 cc
Tween 20™ C ₅₈ H ₁₁₄ O ₂₆ <i>aka</i> polyoxyethylenesorbitanmonolaurate; polysorbate Separate solution diluted to 10% or 5% v/v	0.25 cc

7.3 Processing chemicals

Purity: General Purpose Reagent (GPR) grade *ca.* 98% is adequate.
These quantities suffice to process *ca.* 60 10x8 in. Pt/Pd prints.

Processing Solutions	Quantity
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Ethylenediaminetetraacetic acid, disodium salt 5% w/v $(\text{NaO}_2\text{CCH}_2)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2 \cdot 2\text{H}_2\text{O}$ <i>aka</i> 1,2-Diaminoethanetetraethanoic acid, disodium salt; Disodium EDTA; disodium edetate; http://www.alfa.com/content/msds/english/A15161.pdf	2 litres
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dissolve 100 g of the solid in 2 litres of water

Ethylenediaminetetraacetic acid tetrasodium salt 5% w/v $(\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{Na}))_2 \cdot 2\text{H}_2\text{O}$ <i>aka</i> 1,2-Diaminoethanetetraethanoic acid, tetrasodium salt; Tetrasodium EDTA; tetrasodium edetate	2 litres
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dissolve 100 g of the solid in 2 litres of water

Sodium metabisulphite $\text{Na}_2\text{S}_2\text{O}_5$ 2.5% w/v <i>aka</i> sodium pyrosulphite; sodium disulphite	1 litre
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dissolve 25 g (a level tablespoonful) of the solid in 1 litre of water

Alternatively, sodium sulphite or sodium hydrogen sulphite (sodium bisulphite) or Kodak 'Hypoclear' powder may be used. This solution should be made up fresh for a day's printing, and not stored and re-used.

7.4 Apparatus for preparing sensitizer

Pyrex glass beakers 2 x 100 cc

Measuring cylinder 50 or 100 cc

Scales or chemical balance sensitive to 0.1 g

Glass stirring rod

Conical filter funnel *ca.* 5–6 cm diameter

Filter paper Whatman Grade #1 *ca.* 8–10 cm diameter

Brown glass bottles 3 x 100 cc

Hotplate (or bath of very hot water)

Tungsten lighting to work under, not fluorescent or daylight.

7.5 Equipment for printing

Paper

Glass coating rod

Blotting strips

Syringes – at least 4, calibrated 1 cc, 2 cc and 5 cc

Mixing vessel – small liqueur or ‘shot’ glass

Glass plate – at least 6mm thick

Spirit level

Drafting tape or clips

Print frame – preferably hinged-back

Hygrometer

Cat litter trays – for humidifier enclosures – with lids

UVA light source, such as a domestic ‘solarium’ – facial tanning unit

Timer

Plastic measuring jug 2 litre

Stirrer

Processing dishes (5)

Tongs or plastic gloves

Drying line and pegs or drying screen

7.6 Iron solution preparation

60% w/v ammonium iron(III) oxalate trihydrate (1.40 M)

(Volume 50 cc)

N.B. The following sequence of instructions should be carried out under dim tungsten lighting, not fluorescent or daylight.

- 1 Weigh out 30 g of ammonium iron(III) oxalate trihydrate, $(\text{NH}_4)_3\text{Fe}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$ FW 428.07, into a small (100 cc) Pyrex glass beaker.
- 2 Add exactly 33 cc of pure water (from a measuring cylinder) and stir well to dissolve the solid.
- 3 The solution becomes cold, so gently warm the beaker in a bath of hot water (ca. 50°C) to assist dissolution.
- 4 The solid will dissolve to form an emerald-green solution within 5 minutes. Check the volume is correct, 50 cc, and if not make it up. The solution pH should be ~5.

(Any tiny residue of remaining solid may be ignored.)

- 5 Filter the solution (Whatman #1 filter paper) directly into a clean, dry, brown glass storage bottle, and label and date it appropriately. Store at room temperature in the dark: the shelf life will be several years.

(If, after a few days, a few white needle-like crystals (probably of ammonium oxalate) have appeared, re-filter the solution to remove them. This solution is close to saturation; if cooled below 20°C for a length of time, green crystals may appear: warm gently and swirl to redissolve them.)

7.7 Platinum solution preparation

25% w/v ammonium tetrachloroplatinate(II) (0.67 M)

(Volume 20 cc)

NB. Read the Health and Safety warning in §6.4.

- 1 Weigh out 5 g of ammonium tetrachloroplatinate(II), $(\text{NH}_4)_2\text{PtCl}_4$ FW 372.98, into a small (50–100 cc) Pyrex glass beaker.
- 2 Add 18 cc of pure water from a measuring cylinder and dissolve the solid by stirring at room temperature. The final volume should be exactly 20 cc, if not, make it up.
- 3 Decant the solution directly into a brown glass storage bottle, labelled and dated. (Its pH is ~3).

(Any small amount of yellow precipitate may be ignored.)

- 4 Allow the solution to stand for at least 24 hours before first use.

(The solution should keep for a year or so, but is not stable indefinitely.)

7.8 Palladium solution preparation

19% w/v ammonium tetrachloropalladate(II) (0.67 M)

(Two options – depending on price and availability of chemicals)

EITHER

Method 1 (Volume 26 cc)

- 1 Weigh out 5 g of ammonium tetrachloropalladate(II), $(\text{NH}_4)_2\text{PdCl}_4$ FW 284.29, and transfer into a small (50 cc) measuring cylinder.
- 2 Add ca. 15 cc of pure water to dissolve the solid by stirring at room temperature.
- 3 Make up the solution with pure water to a volume of exactly 26 cc in the measuring cylinder.
- 4 Filter the solution using a small conical funnel and Whatman Grade #1 filter paper, directly into a brown glass storage bottle, stopper and label it.

OR

Method 2 (Volume 25 cc)

- 1 Weigh out accurately 1.8 g of ammonium chloride, NH_4Cl FW 53.49, into a 100 cc Pyrex glass beaker.
- 2 Add 20 cc of pure water and all the solid should dissolve easily.
- 3 Heat the solution to ca. 70°C, and add 3 g of well-powdered palladium(II) chloride, PdCl_2 FW 177.31, a little at a time, with stirring.

(Hazard! Wear a dust mask.)

Keep hot and stir until all the brown solid has dissolved to give a very dark red solution – which may take up to an hour.

(Carefully view the solution from below to see if any solid remains.)

- 4 Allow the solution to cool and transfer it to a small measuring cylinder, and make up to a volume of exactly 25 cc with pure water. Its pH is ~2.
(Use some of this water to wash out any solution left in the beaker.)
- 5 Filter the solution using a small conical funnel and Whatman Grade #1 filter paper, directly into a brown glass storage bottle; stopper and label it.
(This solution is stable indefinitely.)

7.9 Processing solutions

1. Disodium EDTA (~5% w/v)

Dissolve *ca.* 50 g of disodium EDTA in *ca.* 1 litre (1000 cc) of tap water in a large plastic measuring jug with stirring at room temperature.
Capacity ~50 prints 10"x8" per litre.

Alternative formulation using Tetrasodium EDTA

If disodium EDTA is unavailable, and only tetrasodium EDTA on hand, the latter may be effectively converted to the former by the addition of citric acid, (C₆H₈O₇ FW 192.12) to the extent of 31 g of citric acid to each 100 g of tetrasodium EDTA. The presence of the citrate ion can only assist the clearing.

2. Sodium disulphite (~2.5% w/v)

Dissolve *ca.* 25 g (one rounded tablespoonful) of sodium disulphite, (aka sodium metabisulphite, Na₂S₂O₅ FW 190.10) in *ca.* 1000 cc of tap water. Use this solution for one printing session only and discard it. Do not store.

3. Tetrasodium EDTA (~5% w/v)

Dissolve *ca.* 50 g of tetrasodium EDTA in *ca.* 1000 cc of tap water with stirring at room temperature.
Capacity ~100 prints 10"x8" per litre.

Alternative formulations using H₄EDTA

If the only available chemical is the free tetrabasic acid H₄EDTA itself, and not its sodium salts, to make 5% solutions for baths 1 and 3 it may be partially neutralised by any convenient sodium alkali in the following proportions:

Dissolve **one** of the following amounts of alkali per 1000 cc of water, and add ~35 g of H₄EDTA (0.12 moles) in small portions with stirring, allowing (in the case of the carbonates) the effervescence of CO₂ to subside:

Alkali to add to H ₄ EDTA to make:	Na ₂ EDTA	Na ₄ EDTA
Sodium hydroxide NaOH	9.6 g	19.2 g
Sodium carbonate Na ₂ CO ₃ (anhyd.)	12.7 g	25.4 g
Sodium carbonate Na ₂ CO ₃ .10H ₂ O	34.3 g	68.6 g
Sodium bicarbonate NaHCO ₃	20.2 g	40.3 g

Alternative formulation using Disodium EDTA

To convert Na₂EDTA into Na₄EDTA: add ~45 g of it to 9.6 g of NaOH etc., or alkali as above, dissolved in 1 litre of water.

7.10 Suitable modern papers

Do not use "acid free" papers that are alkaline-buffered with chalk (calcium carbonate), which reacts destructively with the sensitizer (§8.6). The best results will be obtained on unbuffered papers such as:

- 'Buxton' or 'Herschel' – handmade by Ruscombe Mill
- Arches Platine
- Weston Diploma Parchment
- Crane's Platinotype, also called Crane's Business Card Stock, Natural or Pearl White Wove
- Wyndstone Vellum (§8.9)
- Hahnemühle Platinum Rag
- Atlantis Silversafe Photostore

If buffered papers are unavoidable, such as Canson Lavis Technique, Fabriano Artístico, or Whatman Watercolour, they should be pre-treated in a bath of dilute (5% v/v) hydrochloric acid to destroy the chalk, then washed for an hour. Recently, a 10% sulphamic acid bath for 20 minutes has been recommended as a convenient substance to decalcify papers.⁶¹⁹ Do not use oxalic acid for this purpose: calcium oxalate is as insoluble as the calcium carbonate that it is intended to remove.⁶²⁰

Do not use gelatin-sized papers such as Arches Aquarelle, Bergger COT320, or Fabriano 5 for platinum-containing prints: gelatin, depending on its quality, tends to inhibit the chemistry of platinum metal formation (§11.5). They may be used for pure palladium prints, upon which gelatin has no adverse effect. Suitable papers for platinum printing are sized with alkylketene dimers (AKD), such as Aquapel™, or with the traditional alum-rosin sizing.

For prints up to 10x8 in. or A4 in size, a paper weight of 160 gsm (grams per square meter, g/m²) is adequate. For larger prints of A3 size, a weight of 240 gsm, or more, will minimise cockling and "bellying" of the coated sheet due to the stresses set up by the hydroexpansion of the cellulose fibres in the wetted area. The sheet will contact the negative better, and be more robust in wet handling.

7.11 Sensitizer composition and image colour

Platinum and palladium solutions may be used separately, or combined in any ratio in the sensitizer in order to fulfill your wishes for the hue and contrast of the finished print:

Palladium yields Van Dyke brown or sepia tones and a softer image, *i.e.* a longer exposure scale, with great delicacy in the high values. The tones are warmer on gelatin-sized papers than on Aquapel-sized. When well-humidified, near-neutral tones can be achieved, provided that exposures are not too short in duration, and little or no Tween surfactant is used – see §11.15.

Platinum yields neutral grey tones and tends to provide a slightly higher contrast (shorter exposure scale) than palladium, and greater maximum density; but the overall speed of printing may be slower, depending on the purity of the paper, which is paramount. If prints in 100% platinum are desired see §7.25.

Platinum-palladium mixtures combine their characteristics proportionally, and offer a useful compromise, but leave an uncertainty about the composition of the image, see §11.4.

7.12 Sensitizer characteristics

For characteristic curves of density vs. log exposure, see §11.6, Fig. 11.3.

The characteristics of some sensitizers are summarised in Table 7.1 below, for reference, showing their dependence on the Relative Humidity (RH%).

- The Relative Speed is arithmetic, referring to middle tones.
- The Exposure Range ($\Delta \log H$) is from fog+0.04 to $0.9D_{\max}$
- Development is in logH units (0.3=1 stop). 0 is total print-out.
- Note that these parameters will vary with the choice of paper.

Sensitizer	RH %	Relative Speed	Expos. Range	Develop-ment	Colour
Platinum	32	1.8	1.5	0.9	warm black
	55	1.7	1.5	0.3	warm black
	80	1.0	1.8	0	neutral
Palladium	32	0.5	2.0	0.4	sepia
	55	1.3	2.2	0.2	vandyke brown
	80	2.5	2.4	0	warm black
Platinum-palladium (3:1)	32	1.2	1.6	0.6	warm black
	55	1.0	2.0	0.1	neutral
	80	1.0	2.2	0	neutral
Platinum-palladium (1:1)	32	1.2	1.6	0.6	warm black
	55	1.0	1.8	0.2	neutral
	80	1.0	2.0	0	neutral

Table 7.1 Characteristics of print-out platinum-palladium sensitizers

It will be noted that with platinum the speed of the sensitizer decreases with increasing relative humidity (RH%), whereas with palladium the converse is true. The possible causes of this counter-intuitive behaviour are discussed in §11.11. The useful consequence of this contrary behaviour, also evident from Table 7.1, is that mixtures of platinum and palladium provide a relative speed that varies rather little with RH.

7.13 Choice of print contrast

Having prepared a negative of approximately the right density range, the contrast may be fine-tuned in the printing process by two main controls: mixing of platinum and palladium in various ratios, or by regulating the humidity of the sensitized paper before exposure. The printing exposure range ($\Delta\log H$) values in the Table indicate the effects of these controls. Mixing the platinum and palladium solutions in the ratio of 3:1, respectively gives a sensitizer with a contrast and speed that are fairly constant over wide variations in humidity (RH 40–70%), and with a long range of well-graduated neutral tones, and good D_{\max} .

A more economic option is to mix the platinum and palladium solutions in equal volumes, ratio 1:1, which will provide a slightly warmer image tone, especially at the lower RH values, and slightly softer contrast.

7.14 Mixing the sensitizer solutions

- **For a palladium print** mix equal volumes of the **iron** and **palladium** solutions, which may be coated immediately.
- **For a platinum print** mix equal volumes of the **iron** and **platinum** solutions; for highest D_{\max} let the mixture mature for one hour in the dark at room temperature before coating.
- **For a platinum-palladium print** you may combine the **platinum** and **palladium** solutions in any proportion: then combine the mixture with an equal volume of **iron** solution. Mixing should be done at room temperature under tungsten lighting. Preferably let the mixture mature for one hour in the dark before coating, though this is not essential.

These small volumes are conveniently measured and delivered by means of disposable calibrated plastic syringes (*without* hypodermic needles!) of capacity e.g. 1, 2, or 5 cc, to match the print size. Dedicate a separate syringe for each solution to avoid cross-contamination of the stock solutions, and use a fourth syringe for delivering the mixed sensitizer onto the paper. A small liqueur glass makes an ideal mixing vessel – provided you give up drinking out of it! Mix the solutions well by drawing the liquid gently in and out of the delivery syringe three times. To ‘mature’ a solution before coating draw it up into a syringe to minimise evaporation, and leave in a dark place. Room temperature should be normal (18–22°C), if too low the sensitizer may crystallize.

7.15 Use of surfactant

Absorbent papers may not require any additional surfactant (wetting agent), but some hard-sized papers, such as Buxton, may yield a better, more uniform coating if a surfactant is used. Tween 20™ (a non-ionic surfactant) may be added to the sensitizer solution before coating to produce a final concentration of ca. 0.25%. Add one drop (0.05 cc) of a 5% stock solution of Tween 20™ for

each cc of sensitizer and mix well (or one drop of 10% per 2 cc). Do not add Tween to the stock sensitizer solution: it doesn't last well, and the appropriate amount will depend upon the paper. It may interact unfavourably with gelatin-sized papers. Tween also tends to promote a warmer colour in palladium.

7.16 Coating by glass rod

Paper which has been stored at low relative humidity (less than 50% RH) may imbibe excessive amounts of sensitizer and coat unevenly. Before coating, it may be advantageous to pre-humidify the sheet to 70–80% RH. As the coating instrument we recommend a thick-walled glass capillary tube, rather than solid rod, because the former is usually manufactured to higher standards of straightness. An external diameter between 6 and 12 mm is suitable. The end portions of the rod should be bent at an angle using a powerful gas torch; a bicycle handlebar shape is simple and ergonomically effective in use. The centre portion of the rod acts as the spreader and is equal in length to the width of the coating area; the limbs serve as handles. This implement must be kept scrupulously clean and free of grease film. An appropriately-sized rod will be needed for each format to be printed. It is usual to make it equal to the shorter dimension of a rectangular frame. A wide uncoated border is recommended to facilitate handling. All manipulation of the sensitized paper can be carried out under dim tungsten lighting, avoiding fluorescent light or daylight.⁶²¹ The detailed procedure now follows:

- (1) If necessary, cut or tear your sheet of paper to a size that allows generous margins around the picture area, but still fits the printing frame.
- (2) Mark the sheet of paper lightly in graphite pencil at the corners of the area to be coated – a template helps. The coating dimensions should be ~1 cm larger than the negative to allow for irregularities. Note the area in m².
- (3) Tape or clip the sheet lightly, at top and bottom, to a very flat level surface: a heavy glass plate is ideal. Use a low-tack tape such as Scotch Removeable 3M811.
- (4) Check with a spirit level that the paper is horizontal left to right; this is critical, so adjust it if necessary by inserting spacers below the glass plate.
- (5) Dust off the surface with a blower brush.
- (6) Draw up the mixed sensitizer into a syringe of appropriate size, and adjust it to the required volume, reading from the bottom of the plunger. A trial volume may be calculated from the average specific coating volume of 30 cubic centimeters per square meter of surface area (30 cc/m²).
- (7) Point the nozzle of the syringe at the bottom left mark, and expel the liquid slowly and gently (use two hands) in an unbroken strip of sensitizer as you move it steadily from left to right across the width of the coating area. For steadiness, touch the paper lightly with the syringe nozzle. Do not be too slow or fussy – irregularities will even out in the coating.
- (8) Hold the spreading rod with one end in each hand, and place the straight central portion onto the paper parallel to, and a little below, the strip of

sensitizer. Then, with moderate pressure, push the spreading rod up into the strip of solution. Pause briefly (2 seconds) while the liquid distributes itself uniformly along the length of the rod, then steadily push the strip of solution up the paper, like a tiny tidal wave running in front of the rod.

- (9) When you reach the pencil marks at the top of the coated area, 'hop' the rod over the strip of solution and pull it back to the bottom of the coating; then hop over the sensitizer strip once more and push it up to repeat the spreading. Just four passes over the paper should suffice for its surface layer to become saturated with a uniform coating of sensitizer. The first pass should be made quite rapidly (3 or 4 seconds) applying moderate pressure to ensure complete wetting of the surface. The last three passes as slowly as possible (10 to 15 seconds each) with very little pressure applied, to allow maximum absorption. At the end of the fourth pass, drag the spreader below the picture area with any excess sensitizer. But if much excess solution remains you can apply two more passes.
- (10) Gently lift off the spreader rod, and soak up any residual liquid left at the bottom of the coating with the edge of a clean strip of blotting paper, to avoid any crystallization that may damage the negative.
- (11) In future coatings, try to "fine tune" your exact coating volume on the basis of experience with your chosen paper, in order to minimise waste.

7.17 *Drying and storage*

It is simplest to let the sensitized paper dry at room temperature and RH, in the dark, for about an hour. Shorter times are possible, but very humid paper may damage precious silver-gelatin negatives, and not lie flat due to swollen fibres. Alternatively, allow a few minutes for the sensitizer to soak in, until the paper surface appears non-reflective, then heat-dry it with an air stream at about 40°C for *ca.* 10 minutes.

The sensitized paper should be used within a few hours; otherwise, it must be stored in a light-tight, air-tight container, in the presence of a desiccant such as silica gel or anhydrous calcium chloride, below 10% RH, in order to prevent chemical fogging. Paper may be stored for six months in this way without loss of quality.

7.18 *Humidifying*

The key to the print-out process of platino-palladiotype lies in controlling the humidity of the sensitized paper just before exposure. The effect of ambient RH on the extent of print-out, colour and contrast is summarised in the Table above, from which you will see that optimum results are obtained between 50% and 80% ambient RH. Below 50% RH there is only partial printout and considerable development, above 80% RH the maximum density of the image may tend to weaken because the sensitizer diffuses too deeply into the paper. If you have a hygrometer, you can simply make use of the prevailing relative humidity (if suitable) to achieve a predictable result by hanging the paper in a dark place at room temperature (*ca.* 20°C) for an hour or two before exposure.

Greater control, however, is provided by a humidifying tank *i.e.* a fairly shallow opaque plastic box larger than the paper size, provided with a flat lid, also opaque, offering a reasonably air-tight seal. Cat litter trays are ideal for this purpose; photographic dishes are too shallow and have a lip which makes sealing difficult. If it is desired to maintain very low RH, it is best to fit a strip of sponge draught seal around the rim of the tray and use clips to secure the lid to it under slight pressure. The sheet of sensitized paper is held securely on the underside of the lid, by two strips of self-adhesive magnetic tape, which is quick, clean, easy to use, and does not mark the paper. The coated side faces down, above – but not in contact with – a saturated aqueous solution which provides an atmosphere of constant, known relative humidity (see §11.16). The most useful saturated solutions are: ammonium chloride (RH 80%); sodium chloride or common salt (RH 76%) and calcium nitrate tetrahydrate (RH 56%).

It is important that there should be excess solid salt in contact with its saturated solution, and that the paper should be evenly exposed to the vapour. The time of exposure in the humidifying tank should not be less than half an hour, to achieve evenness; the upper time limit can be a few hours.

A simpler method of humidifying is to use pure water in the tank, which therefore contains an atmosphere of 100% RH; but in this case the timing of the humidification is critical: from 5 to 20 minutes for a warm-toned result; a longer humidification of 30 to 40 minutes in the water vapour will yield fuller print-out and a colder image tone. Humidification at RH 100% for more than one hour may lead to weakening of the image density, and clearing problems. Over-humidified paper may also damage negatives during contact printing.

7.19 Ultraviolet light sources

Any light source with a substantial ultra-violet content will serve for printing the iron-based processes. However, sources like 'sun-guns' and quartz-halogen lamps also emit infra-red radiation, which has the undesirable effect of heating the paper as the exposure proceeds. The best sources are fluorescent-coated mercury-discharge tubes, emitting mostly the so-called 'long-wave ultra-violet' (or UVA, with a wavelength range of 320–400 nm) with a maximum output around a wavelength of 365 nm. There is no advantage, and much additional risk, in employing the more dangerous short-wave ultraviolet mercury lamps which rapidly damage eyes and living tissue.⁶²² Long-wave UVA lamps are marketed for graphic arts purposes as well as for domestic sun-tanning. The following UV sources are listed in ascending order of cost:

1 The sun. This is free, but an uncertain and variable source in many locations. The sun is nearly a point source giving high acutance because it subtends a 0.5 degree angle only. In intensity the sun is about four times faster than a small UV source like no. 4. There is a considerable heating effect which may affect lengthy exposures. The north summer sky is a diffuse source with a wide aspect like a 'light bed', no. 4. Its intensity is about 3 stops (8x) less than direct sun with about half the speed of no. 4.

2 Small domestic sunlamps such as the Pifco 300 watt UV lamp No. 1012. These should be used at a distance of about 30 to 50 cm from the printing frame, providing about half the speed of no. 4.

3 Mercury discharge reprographic lamps, such as the Philips HPR 125W, used at a distance of about 30 cm from the frame.

4 A convenient unit such as that once marketed by Gordon Audio-Visual as a Diazo printer. This provides a 'light bed' of four Philips fluorescent tubes, type TLADK 30W/05 UV, distant about 8 cm from the print, and is adequate for an image up to 25x30 cm. It delivers a UV energy of 50 W m⁻² at the print surface.

5 A similar array can be made quite cheaply by purchasing from a lighting supply house a commercial luminaire fitting, which is equipped with all the sockets and control gear to take four 600 mm fluorescent tubes. UVA tubes marketed as 'insect attractors' are suitable, but not the 'super actinic' variety of plant or aquarium light. Filtered BLB 'black-light blue' lamps will work, but less efficiently.

6 A domestic suntan bed – for large prints. The 'facial solarium' is a smaller and more convenient version of this type of source such as the Philips 'Cleo', fig. 6.4, §6.13, which uses six UVA fluorescent tubes (actinic/09) with a power of 20 watts each, and easily covers an area 30x35 cm.

7 If cost is no object, a commercial mercury-arc exposure system such as those manufactured for the graphic arts and screen printing industry. The NuArc is a popular model for alternative printing and is fitted with a vacuum easel. The aspect of this UV light source is quite small, subtending about a 5 degree angle at the platen, so it is good for maintaining high acutance in the image. Exposure units like the NuArc are fitted with a built-in light integrator which measures the intensity continuously and multiplies it by the elapsed time, so accumulating the overall dose of light which is read out in units of exposure, not units of time. This is particularly necessary because the emission of the small high intensity mercury arcs used tends to vary with time.

8 UV light-emitting diodes (LED) have recently become available for adoption as siderotype printing sources, and they may well prove the most stable, convenient and long-lived of all sources. However the commonest variety only have peak emissivity at rather long UV wavelengths, ca. 390 nm, which is less efficient than the mercury emission at 365 nm for siderotypes.

The considerations regarding image sharpness set out below should be borne in mind when choosing a light source. Whatever source you use, be sure to protect your eyes with appropriate UV-absorbing goggles. All the sources depend on discharges in mercury vapour and such light sources do not emit their full intensity on switch-on from cold – they warm up over a period of time while the mercury vapourises, and the light intensity increases with time, until a steady state is reached. If that time interval is significant compared with the duration of exposure it can lead to inconsistencies unless the lamps are warmed up for 5 minutes or so in the absence of any sensitive material. Then they may be briefly switched off and the print frame with negative and paper fairly quickly inserted, then the exposure is made using warm lamps.

The geometry of the light source can affect the image acutance in contact printing: if **gaps** are formed between negative and sensitized surface, they may be wide enough to **blur** the acutance or resolution of the image, to an extent that depends on the geometry of the light source. The **blur** is the width of the penumbra (fuzzy zone) between light and full shadow at any edge within the

image, and depends on the ratio of size to distance of the light source. If the largest linear dimension of the light source is w , and its distance from the print is d , then w/d is the **aspect value** of the light source. By similar triangles:

$$\text{blur} = \text{gap} \times \text{aspect value of light source}$$

The human eye at its near-point (ca. 250 mm) can resolve ~0.1 mm, but 0.25 mm is taken to be acceptably 'sharp' in calculating the 'depth of field' of lenses. We may take 0.3 mm of blur as the onset of a 'fuzzy' or 'soft' image. The blur generated by various light sources is summarised in Table 7.2:

Light Source	Aspect value w/d	Blur in mm for a gap of	
		0.1 mm	0.5 mm
Sun	0.01	0.001	0.005
NuArc 2125	0.1	0.01	0.05
'Light bed' or sky	4	0.4	2.0

Table 7.2 Blurring of image caused by geometry of various light sources

7.20 Exposure and printing frames

Negatives should have a long density range (at UVA wavelengths): at least 1.8 for platinum and as much as 2.4 for palladium, to produce a full tonal range in the print – as for my other siderotype processes. With the widespread use of digital internegatives made on ink-jet printers, optical densitometry is of little value, for reasons given in Appendix IV, so the correct density range is arrived at empirically. Exposure time will be a few minutes under an average UVA light source – e.g. using a UVA facial solarium (§6.13) of 120 watts it will be about 5 minutes. With an 800 watt HID UV lamp in a NuArc printer and digital negatives, exposure is ca. 40 seconds.

Since this is a print-out process, a hinged-back contact printing frame (see §6.12) enables intermediate inspection of the result without loss of registration. Under conditions of full print-out (ca. 80% RH) one can continue exposing until the highlight detail is resolved; the shadows will not block up totally, as they do in development papers, because the printing-out process has a self-masking action in regions of high print density.

In all the siderotype processes, including platinum-palladium, one of the by-products of the photochemical reaction is carbon dioxide gas (§11.1). The quantity of this gas so produced can be calculated, as follows:

Assuming a specific coating volume of 25 cm³/m² of sensitizer, of concentration 0.7 molar in ferrioxalate, complete exposure to transform all the Fe(III) to Fe(II) would release:

$$0.025 \times 0.7 = 0.0175 \text{ moles of CO}_2 / \text{m}^2.$$

The volume of this amount of gas is:

$$0.0175 \times 22400 = 392 \text{ cm}^3 \text{ CO}_2 / \text{m}^2 \text{ at S.T.P.}$$

The 'layer thickness' of this volume of gas over an area of 1 m² is:

$392/10,000 \text{ cm} = 0.0392 \text{ cm} = 0.4 \text{ mm}$ approximately.

This is a 'worst case' scenario of maximum exposure; actual exposures will be less by several stops.

A separation of negative and paper by 0.1 mm is sufficient to perceptibly 'blur' an image printed by a UV 'light bed' (Table 7.2), showing that if the gas is trapped as a bubble between negative and paper the gap may cause a loss of image acutance (edge-sharpness or resolution) in regions of high local contrast, depending on the nature of the light source. It is only likely to cause a visible problem with extended sources, such as a solarium. Clear evidence for this has been obtained by the author.⁶²³ It is therefore important to the quality of the print that this gas should be able to find a pathway to diffuse out from the sensitized surface. The permeability of the printing paper should be sufficient to allow passage of the gas through to its *verso*, and this militates against the use of surface sizing agents such as gelatin on the paper, which tends to block the pores between the fibres. Moreover the printing paper should *not* be backed by an impervious plastic sheet in the printing frame, but only with a felt blanket of the kind used by papermakers, or other material permeable to gases, such as a porous plastic sheet, which will absorb the CO₂.

7.21 Negative masking

The author believes that it is preferable to mask the borders of the coated area lying outside the negative to give a clean edge to the image, rather than to expose them showing the rough edges left by brush strokes or passes of the glass rod. This is achieved by adhering strips of UV absorbing 'Ruby-Lith' to the interior of the glass. Here are the three reasons for my preference – aesthetic, technical, and practical:

Aesthetically, it seems unnecessary to "show the brushmarks" in order to prove that it's a handmade print. Connoisseurs will already know that anyway. Moreover, an erratic, wide black border imposes a strong peripheral distraction from the image content. The formal, geometrical qualities of the rectangular frame have the time-honoured virtue of being unpretentious.

The technical reason is most important: the masked borders that have been coated with sensitizer but remain unexposed, provide a direct visual check, by comparison with the adjacent uncoated margins of the paper sheet, as to the completeness of clearing excess chemicals from the print during the wet processing. If the borders are not masked, but exposed and darkened, one can never be sure if the print has been fully cleared and its highlights remain undegraded. It can be a cruelly demanding test – but very desirable in the interests of archival permanence!

In practical terms, if there is a large non-image area of redundant sensitizer in the borders which is heavily exposed, during wet processing the dense photoproduct may bleed into light image areas like sky, and ruin the print. Moreover the needless evolution of extra carbon dioxide gas may jeopardise the print acutance, as described above. Masking the print with 'Rubylith' or black polythene costs nothing except a little care and precision – hallmarks of good craftsmanship. If digital ink-jet negatives are used they may be printed with wide opaque borders to provide a mask.

7.22 *Wet processing procedure*

The chemical logic which explains the following procedure is set out in §10.10.

1 “Steam” the print (an optional step: ‘post-hydration’) 1–2 minutes

To enhance the gradation in the high values, especially if print-out is not complete, expose the print surface uniformly to water vapour over a tray of water at *ca.* 40°C. Then immerse it in the following wet-processing baths, face-down if it floats, or face-up if it sinks, with intermittent agitation:

2 Develop in disodium EDTA (5% w/v) 10 minutes

It is important that this first bath should be acidic, pH ~3–4. Do not use tetrasodium EDTA (pH ~9). Its capacity is *ca.* 60 10x8 in. prints. When spent, this bath should be saved for recovery of precious metals.

3 Rinse in water half minute

4 Clear in sodium disulphite (2.5% w/v) 10 minutes

This disulphite bath does not keep, so should not be stored and re-used, but made up fresh for each printing session.

5 Rinse in water half minute

6 Clear in tetrasodium EDTA (5% w/v) 10 minutes

The capacity of this two litre bath is at least 60 10x8 in. prints.

7 Wash in running water for a minimum of 30 minutes

If there is a water shortage, use at least three fresh static baths.

8 Drain face out, on a near-vertical sheet of Perspex 10 minutes

9 Dry at room temperature on a horizontal plastic or fibreglass fine screen.

N.B. Safety warning. Do not allow the processing solutions, especially bath 2, to come in contact with your skin: use print tongs or gloves.

Examine the print for any yellow stain of residual iron in the borders of unexposed sensitizer; use a bluish light. If stain is present, prolong Bath 6.

In a 100% platinum print the print-out is less vigorous, especially at low RH. Better quality may result if the more energetic platinotype developer, 30% w/v potassium oxalate solution, is used for bath 2, see §7.25.

7.23 *Finishing, permanence and stability*

The print is easy to retouch using permanent artist-quality watercolour pigments. Platino-palladiotypes are highly lightfast and robustly resistant to all contaminants likely to arise in a normal environment. There is no convenient reagent for dissolving platinum images. Palladium is slightly attacked by dilute hydrochloric acid in air, but dilute hydrobromic acid is much more effective as a print “reducer” (*i.e.* oxidising agent): palladium images may be etched by dilute hydrobromic acid (1% to 10% v/v depending on the rate desired), and the action can be accelerated further by adding either ferric bromide (up to 5%) or a little potassium bromate to the HBr. The “reducing” action appears to be “proportional” in its effect across the density scale.

7.24 Workflow for platino-palladiotype

1. **Unbuffered paper preparation:** pre-humidified to 70–80% RH. Choose side, wire or felt, and mark up coating area
2. **Mix sensitizer:** measure and mix equal volumes of iron and platinum+palladium solutions; add Tween to ca. 0.2% if needed
3. **Coat paper:** ~1.5 cc per 10x8 in. ~5 ‘passes’ of rod
4. **Dry:** 1–2 hours at room temperature, or hot air for 10 minutes
5. **Negative:** density range ~2–2.4 in the UVA
6. **Humidify coating:** in controlled RH box (80% for full print-out)
7. **Expose:** to UVA source: print-out until highlights just visible
8. **“Steam”** the print over 40°C water for 2 minutes – optional
9. **Develop and clear #1:** Disodium EDTA 5% for 10 minutes
10. **Rinse** in water half minute
11. **Reduce and clear #2:** Sodium disulphite 2.5% for 10 minutes
12. **Rinse** in water half minute
13. **Final clear #3:** Tetrasodium EDTA 5% for 10 minutes
14. **Wash:** at least 30 minutes or 3 static baths
15. **Drain, dry and press flat**

7.25 *Printing in 100% Platinum*

With a pure platinum sensitizer the print-out is less vigorous, the reactions are slower, and special care is needed to achieve the best print quality. The cardinal points to observe are as follows:

- The choice of paper is critical. It must contain no trace of gelatin size (see §5.2, 7.6, 8.5, 11.5) or alkaline buffer (calcium carbonate, see §8.6). Several of the Crane's papers (Crest parchment, AS8111, Cover Natural White) work well, as do Buxton and Herschel handmade papers, Arches platine. Wyndstone Vellum and other 'parchmentized' papers may also give fine results.
- Newly-mixed sensitizer should be allowed to 'mature' in the dark for an hour before coating, to obtain the best D_{\max} . This need not interrupt the flow of work, because this mixed sensitizer appears to be stable for years, so a batch can be prepared in advance of printing sessions.
- A generous post-hydration (after exposure, but before immersion in the wet processing baths) will give the image the best chance to complete its print-out. 20–30 minutes over water at room temperature, or 2–4 minutes over water at 40°C are recommended.
- If highlight detail is still deficient, or 'grain' evident due to the fibrous structure of the paper, then the first processing bath (disodium EDTA) may be replaced with the more energetic traditional platinotype developer bath of ~30% potassium oxalate (poisonous!). It may even be used hot.
- Although it is a 'cheat', adding just one drop of palladium solution, §7.8, to the sensitizer can improve print-out. It appears to work as a catalyst. Re-used 'developer', that may contain some palladium, probably also helps in this way.
- The judicious use of Tween 20 can be beneficial to assist the sensitizer penetrate the paper fibres and smooth out the tones. The optimum concentration depends on the chosen paper. Tween does not keep very well in dilute solution. It is best to make up a 10% solution in distilled water as stock: one drop (ca. 0.05 cc) of this per 1 cc of sensitizer gives a final Tween concentration of ca. 0.5%. Less than this may suffice.

8. Cellulose Chemistry and Suitable Papers

In the siderotype processes the paper base cannot be regarded simply as an inert substrate, as it is in commercial silver–gelatin photographic papers and other sensitized papers that involve a colloidal binder layer in a laminar structure. Rather, the paper fibres must be viewed as a potentially reactive host matrix for the sensitizer ions, especially those with a propensity for hydrogen-bond formation, such as $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ or aquated derivatives thereof, like $\text{Fe}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$, which may be wholly or partially chemisorbed onto the cellulose molecules. The paper is therefore a chemically reactive component in the process which deserves close consideration if we are to understand its influence on the image qualities.

8.1 Molecular structure and morphology of cellulose

Paper consists primarily of a web of the fibrous natural product, cellulose, interlocked by hydrogen-bonding.⁶²⁴ Cellulose is the chief constituent of all plant tissues. The purest papers are made from cotton linters, which are constituted of >98% α -cellulose, which is a polymeric carbohydrate, with empirical formula approximately CH_2O , but is more precisely described chemically as a polysaccharide, a linear polymer (β -1,4 linked) of the sugar hexose, β -D-glucopyranose ($\text{C}_6\text{H}_{12}\text{O}_6$),⁶²⁵ each molecule of which loses a water molecule (H_2O) in the process of forming an ether linkage ($-\text{C}-\text{O}-\text{C}-$) to the next, so the formula of cellulose is $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ the polymer containing ca. $n = 15,000$ of these monomer units in the strong, long-chain form of cellulose, known as α -cellulose.⁶²⁶ (Figure 8.1)

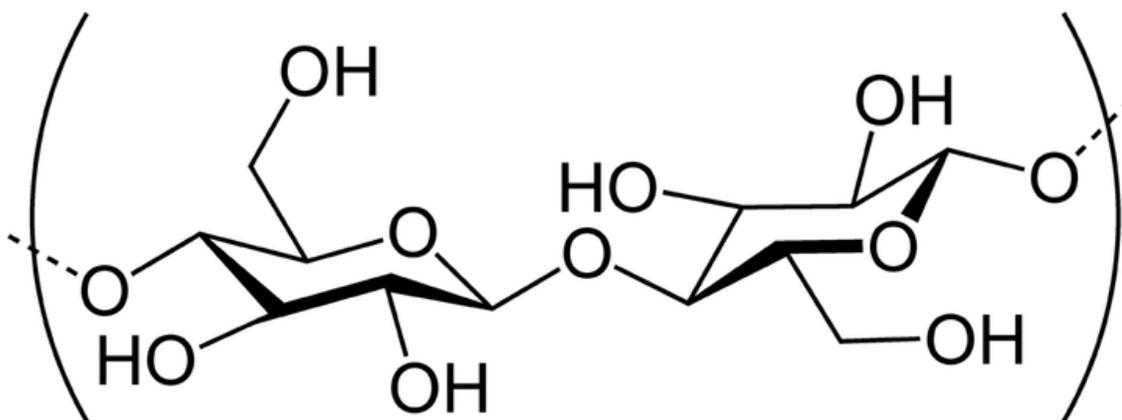


Fig. 8.1 Structure of the basic repeat unit of cellulose $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ called 'cellobiose'.

Cellulose is vulnerable to acids, which split the 1,4 ether linkages, restoring the lost water molecules as hydroxyl groups ($-\text{C}-\text{OH}$ $\text{HO}-\text{C}-$), and thus cause scission of the chains, and consequent embrittlement of the paper

sheet. The polysaccharide chains hydrogen-bond laterally, (Figure 8.2) with the inclusion of some water molecules, so the cellulose structure can display both crystalline and amorphous regions.⁶²⁷

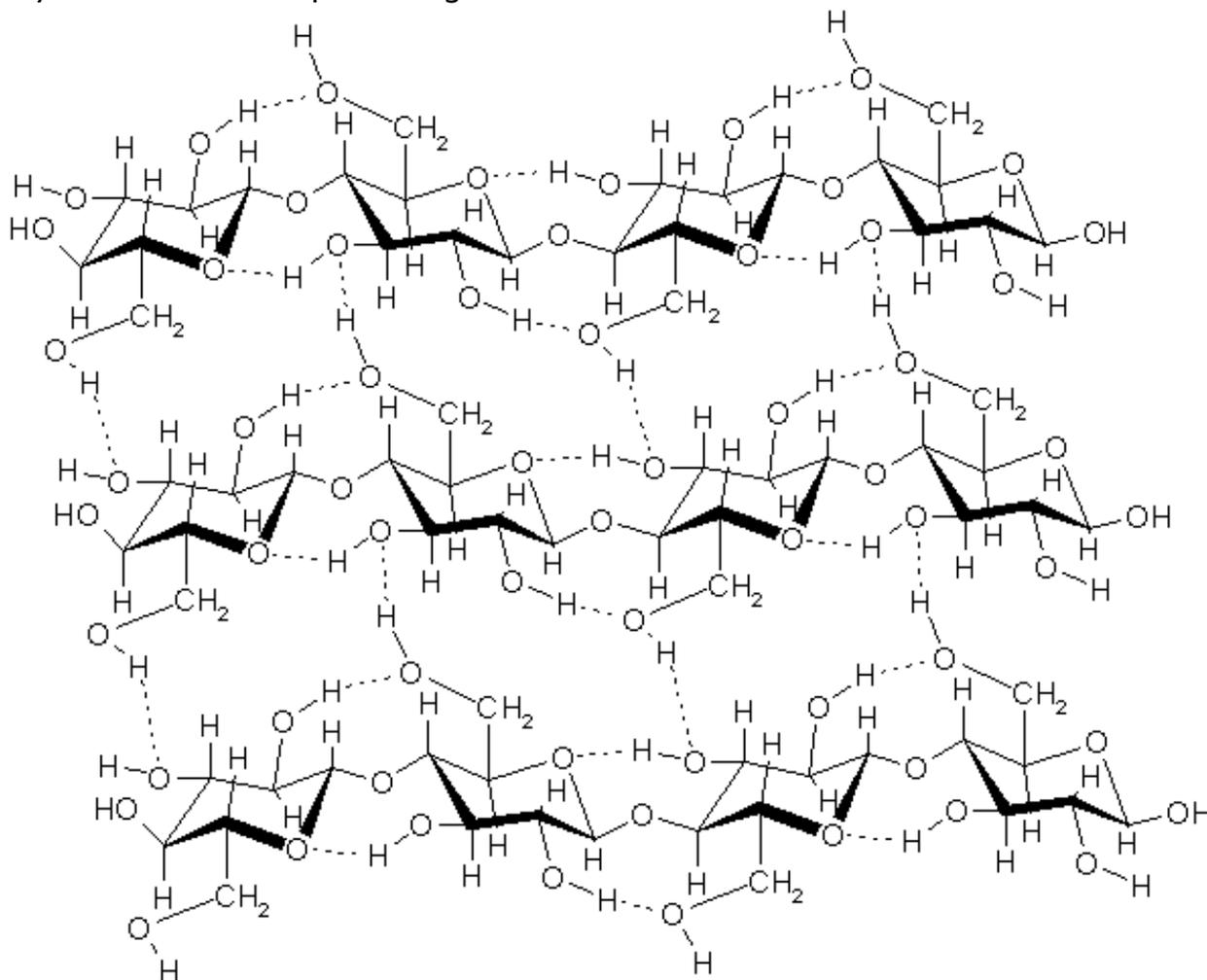


Fig. 8.2 Structure of cellulose showing lateral chain hydrogen-bonding

The morphology of cellulose displays an ascending scale of fibrous aggregation: the individual cellulose molecules cohere into bundles called microfibrils, each containing about 100 parallel molecular chains, held together largely by the hydrogen-bonding between their polar hydroxyl groups. The microfibrils, of dimensions *ca.* 10 x 3.5 nm in cross section and *ca.* 1000 nm (1 μm) long, which can only be seen with an electron microscope, cohere into fibrils, *ca.* 0.5 μm thick and 100 μm long, which comprise the cell walls and are visible in a light microscope; these in turn bundle together to form the visible plant fibre or 'hair', *ca.* 40 μm thick and 1 cm or more long. The cellulose fibres themselves have a complex morphology at the microscopic level, providing an extremely heterogeneous (but aesthetically pleasing!) material, see §8.5.

Cotton is a seed fibre from the seed hairs of the Cotton plant *Gossypium hirsutum*. The fibre has an average length of 25 mm and a width of 0.019 mm. Its appearance is of a flat ribbon with an internal cavity (the *lumen*), rather like a

deflated inner-tube of a bicycle tyre, which appears twisted in the unprocessed state, figure 8.3.⁶²⁸

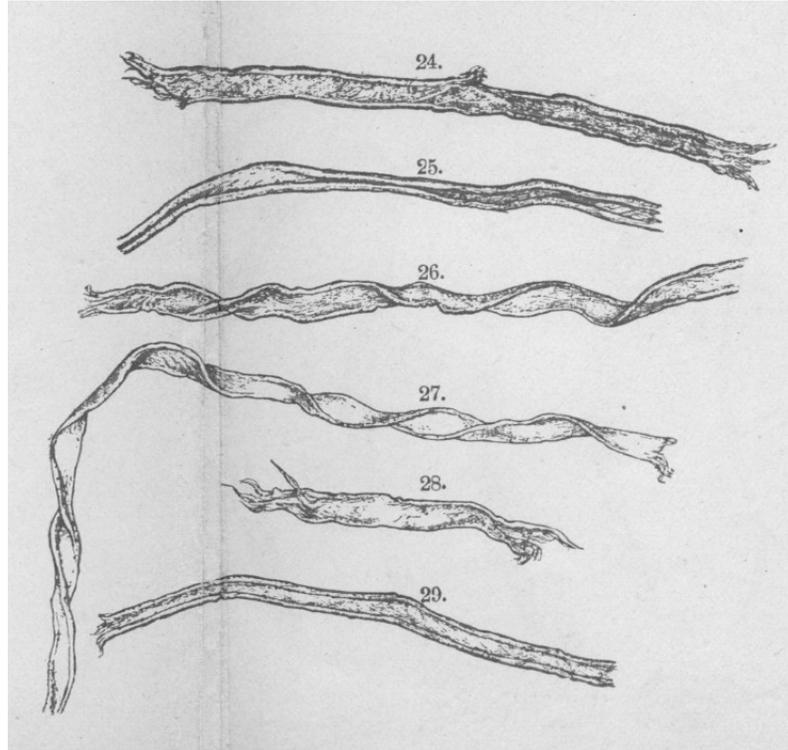


Fig. 8.3 Cotton fibres

8.2 Water content of cellulose

Cellulose itself naturally absorbs water from a normal humid atmosphere to a degree that is well-documented, but the concentration of water in the paper fibres will also depend on the other chemicals present in the sensitizer, especially on the cations used for the complex salts of iron and the noble metal, which may confer hygroscopic or deliquescent properties on the sensitizer. If the sensitized paper is not completely heat-dried, but allowed to equilibrate at ambient RH, then it will also contain significant amounts of absorbed water, as indicated by the cellulose/water absorption curve, figure 8.4.⁶²⁹ For instance, paper that has been conditioned in an environment with a moisture content of *ca.* 70% relative humidity (R.H.) will contain an amount of water in its fibres *ca.* 8% by weight.

There are three distinct regions to this curve, as the humidity increases: initially there is a small but sharp rise corresponding to the bound water that is chemisorbed strongly onto the cellulose; this is followed by a long, gradual, and nearly linear uptake corresponding to the interfibrillar water; finally there is a steep rise, without obvious limit, when the paper imbibes copious amounts of water into its capillary pores at RH values approaching 100%. It is evident that there is a hysteresis or lag in the takeup of water, because the curve for desorption is not coincident with that for absorption, but retains an excess of water.

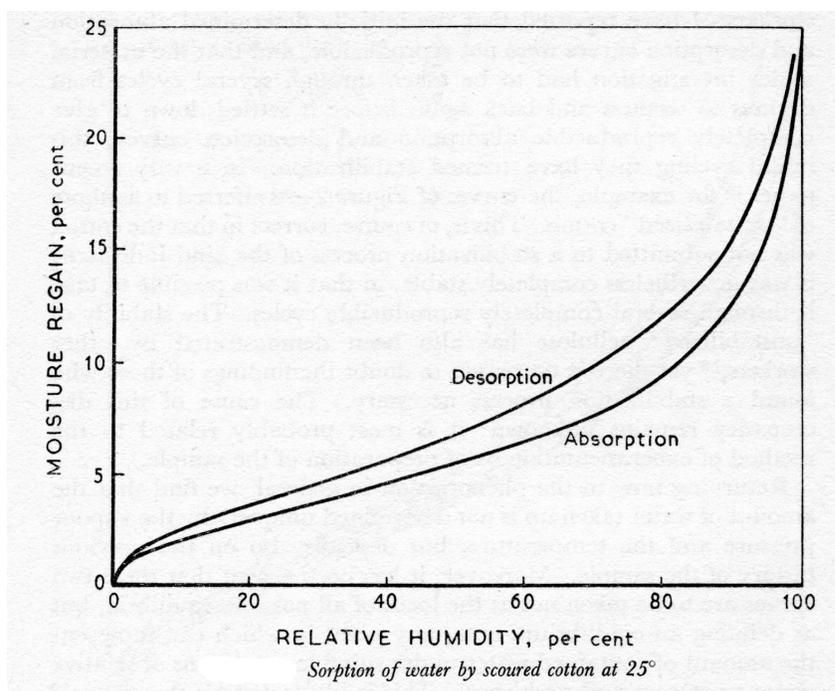


Fig. 8.4 Water absorption by cellulose: dependence on RH

Recalling the microporous structure of cellulose fibres described above; under conditions of high relative humidity, *ca.* 70%, we can calculate that the amount of water hydrogen-bonded within the amorphous regions of the cellulose structure is about ten molecules of water locally to each one of trisoxalatoferate(III) sensitizer. This is sufficient to confer a limited mobility on the iron(II) photoproduct in the interfibrillar space, which facilitates the image-forming redox reaction to reduce the noble metal complex; yet the sheet still 'rattles' and is, to all appearances, dry. Thus the final image is printed out during the exposure, before the wet processing procedure designed to remove excess chemicals. In contrast, if the sensitized paper is thoroughly desiccated there is no print-out and the image is only obtained upon wet development. It should be realised that, in order to provide sufficient water molecules within the fibres of the paper sheet for this short-range diffusion of ions to occur, the paper does not have to be wet, or even perceptibly damp.

Performing photochemistry in paper can be further complicated by the presence of various manufacturers' additives: sizing agents, fillers, buffers, retention and wet strength agents, dyes, pigments and optical brightening agents. It is not sufficient, as in paper chromatography, just to employ a completely pure cellulose paper; the presence of a sizing agent, for example, is essential in order to localise the sensitizer and consequent image in the surface fibres.

The direct absorption of liquid water by penetration of the surface of a sheet is an important property of paper, for many purposes, and its measurement is one of the basic tests of the papermaking industry, called the Cobb test, which has been accepted as a TAPPI standard (T441 m-40).⁶³⁰ Under specified conditions of pressure, temperature and time, the weight of water

taken up by a sheet in contact with pure liquid water is expressed in grams per square meter of surface, g/m^2 .⁶³¹ This is effectively the same (at 21 C) as the volume taken up per square meter: cm^3/m^2 , which we refer to elsewhere as the *specific coating volume*, when the liquid is the sensitizer solution, see §6.10. The Cobb test time can vary as a parameter from 15 seconds to 5 minutes, but 30 or 60 seconds is most usual. The Cobb test values in table 8.1 (here for 30 seconds exposure) measure the effectiveness of the sizing agent to inhibit the uptake of water, thus:

Sizing	Cobb ₃₀ value g/m^2
Normal beater sizing	10
Half sizing	20–30
Quarter sizing	30–40
Slack sizing	>45

Table 8.1 Cobb test values for various sizings

The absorption of water is also found to be proportional to the square root of the time of exposure to the liquid.

8.3 Physical chemistry of photosensitised cellulose

The central problem in formulating a chemical model for the platinotype or palladiotype process lies in deciding what phase is appropriate to describe the state of the photosensitive material after its aqueous solution has been imbibed into the fibres of a cellulose paper substrate and then dried to a prescribed degree. If it is fully dehydrated, as in the traditional method, it probably takes a microcrystalline form comprising more than one solid phase. It was found that when the iron to palladium ratio is high, a single solid phase is obtained consisting of palladium-doped ferrioxalate crystals; in this special case the photochemical reaction may then be modelled by a solid state process involving the conduction band of this single phase.⁶³²

However, this description does not seem applicable to the conditions of the present work in which the molar ratio of iron to palladium has approximately the stoichiometric value of 2 : 1. In a dry sensitized layer mixed microcrystals probably predominate, so the only reaction that can take place during the exposure is the photoreduction of iron(III) in the solid ferrioxalate complex. The resulting colour change is slight, with only the shadow tones of the image becoming discernable. Precipitation of the bulk of the platinum or palladium metal does not occur until the exposed paper is immersed in a "developer", *i.e.* an aqueous solution that mobilises the ions sufficiently for the redox reaction to proceed. In the traditional method of platinotype using a dried iron(III) oxalate sensitizer, the photoproduct is the insoluble iron(II) oxalate, FeC_2O_4 ; this is rendered soluble by complexation, accordingly, the traditional developers contained alkali metal oxalates, and so permit reduction to take place. Other chelating ligands that bind strongly to iron(III) and maintain a low

iron(III)/iron(II) redox potential will also act as "developing" agents: in the present work, disodium ethylenediaminetetraacetate (Na₂EDTA) was used in preference to oxalate for reasons described in §10.9.

If the trisoxalatoferate(III) anion is used for the sensitizer, rather than iron(III) oxalate, the photochemistry is somewhat different. Simple iron(II) oxalate, FeC₂O₄, is not the initial photoproduct,⁶³³ but instead an iron(II) complex, such as Fe(C₂O₄)₂(H₂O)₂²⁻ or possibly a dimeric species such as Fe₂(C₂O₄)₅⁶⁻, is formed, both of which are quite soluble in water. A "developer" as such is not strictly needed, and the presence of water alone suffices to bring about reduction of the platinum(II). Nonetheless there are advantages in retaining the use of a chelating agent such as disodium ethylenediaminetetraacetate in the wet processing procedure, since it is also very effective in removing excess unreacted iron(III) from the paper. To provide this water, there are two main options, development and printout:

- to use an aqueous processing bath to develop the image *after* the exposure. The meaning of "development" here is rather different from the significance that it carries in conventional silver–gelatin processing. There is no amplification of the effects of the light, and no binder is present, the reaction occurs in solution, not to a latent image in the solid halide.
- to ensure that sufficient moisture is present in the paper fibres in the first place, to enable ion–migration and print–out *during* the exposure.

This behaviour inclines one towards a view of the sensitized layer in humidified cellulose paper as a quasi–solution state of partially chemisorbed ions having a limited mobility in a local aqueous environment. This is in marked contrast to the model appropriate for silver halide "emulsions" where the photosensitive material in the microcrystalline solid phase is suspended in a binder gel. Our understanding of this quasi–solution state is probably now only at the same stage as the understanding of silver–gelatin emulsions was fifty years ago, because relatively little work has yet been done on the study of inorganic ions adsorbed – or chemisorbed – on cellulose.

The density of 'unfilled' paper is *ca.* 0.75 g/cm³, whereas that of crystalline cellulose is *ca.* 1.5 g/cm³: this tells us immediately that paper is about 50% by volume empty space – presumably occupied by air – a void that can be partially filled by liquids being imbibed through the pores. There are two interconnected systems of pores within the structure of cellulose paper:

The macroporous structure consists of the capillary channels between the cellulose fibres, easily visible with a hand lens. These pores provide a route for the imbibed fluid into the interior, but this space is not useful for retaining nanoparticle image substances, because their particles will easily be washed out of these regions in the wet processing. Surface sizing, *e.g.* with gelatin, tends to block these channels.

The microporous structure within the cellulose fibres is provided by gaps between the fibrils that make them up. This region, known as the *interfibrillar space*, can effectively trap the nanoparticles of image substance that are formed within it. Penetration of the interfibrillar space of the cellulose structure by the sensitizer solution is therefore of paramount importance, if the image is not to wash away in the wet processing. Surfactants can play an important role here.

In practice, not all of the 50% volume is accessible: pure cellulose paper is usually found to absorb *ca.* 40% of its own weight of water, thus a volume of 1 cm³ of 'waterleaf' paper, weighing 0.75 g, can absorb a maximum of ~0.3 g (= 0.3 cm³) of water which is 30% by volume. The volume of sensitizer applicable in a coating may thus be related to the likely depth to which the solution penetrates the paper. Experimentally, the coating of an internally-sized (AKD) paper by the rod method, see §7.16, is found to use *ca.* 1.5 cm³ of sensitizer to cover the area of an A4 sheet, which is 1/16th of a square meter. The specific coating volume, per unit area of surface, is therefore in the order of 16 x 1.5 = 24 cm³/m², which is comparable with the Cobb value (Table 8.1) for 'half-sized' paper. This would correspond to a 'layer' of pure liquid of thickness 24 µm (*ca.* 1/1000 inch) over an area of 1 m². But saturation of the cellulose structure by liquid only occupies *ca.* 30% of its volume, so the thickness of the layer of paper that is penetrated by sensitizer should be 24/0.3 = 80 µm or 0.08 mm. This calculated thickness of the sensitized layer appears to agree broadly with microscopic measurements made on actual coatings. It is also an indicator of the optical resolution that can be expected for prints made on this substrate. However, electron microscopy of transverse sections of actual Pt/Pd prints indicates that the nanoparticles of image metal are largely confined to a region extending only 10–20 µm deep from the surface.⁶³⁴ This suggests that the imbibed sensitizer is not being used to best efficiency in the exposure of an image on such paper, and a considerable amount of it is not reached by the UV light and must go to waste even in the areas of maximum density.

For a satisfactory coating process of plain paper with sensitizer solution, the critical factor is the rate of absorption of the liquid into the interfibrillar spaces of the cellulose web, a rate that results from a balance between the hydrophobic sizing of the fibres and the rheology of the solution – its surface tension, contact angle, viscosity and density – which may be influenced by surfactants. Too rapid an absorption makes uniform coating of the picture area impossible; too slow an absorption leaves a pool of liquid sensitizer on the surface that will evaporate and form crystals, which seriously compromise the image quality.

8.4 Development versus print-out processes

The traditional iron-based processes employing ferric oxalate (iron(III) oxalate) must be wet-developed, because the photoproduct from this salt is insoluble, ferrous oxalate (iron(II) oxalate), which needs a strong solution of oxalate ions, or other complexing agent, to solubilise it for reaction. In contrast, the print-out processes employ a salt of the ferrioxalate anion (e.g. ammonium iron(III) oxalate). The photoproduct in this case is a soluble iron(II) oxalato-complex, which is reactive enough to reduce the noble metal salt directly, without a 'developer' solution, provided that there is sufficient water present in the paper to facilitate local ion mobility. Many printers find this a more satisfactory way to proceed, because it confers all the benefits of a print-out image, which will be considered below.

The benefit of allowing the image to form by print-out is that no chemicals are lost from the paper at this important stage, and a very complete and

permanent printed-out image can be obtained. On the other hand, as soon as an exposed paper is immersed in a wet-processing bath – a water solution intended to develop the image and clear the excess chemicals – then the water-soluble constituents of the exposed sensitizer begin to leach out of the paper fibres into the bulk of the processing solution, where they are diluted and lost for imaging purposes. If the reaction between the photochemicals to form the image substance takes place as slowly as this washing-out of them, then the image will obviously be weak and incomplete. This is the besetting problem of the traditional platinotype process, where the chemistry of the redox reaction is intrinsically slow, and requires a developing agent to solubilise the iron(II) photoproduct (ferrous oxalate); however, as soon as the print is immersed in an aqueous developer bath, the image-forming chemicals begin to dissolve out before they can fully react, leaving a weak and fibrous or grainy image.

Four strategies have been tried to counter this problem:

- the redox reaction is speeded up by using hot developer (Willis's 'hot-bath' platinotype);
- the exposed sensitizer is induced to reside longer within the fibres and resist leaching-out, by a judicious choice of sizing agents (Willis's use of alum-rosin sized paper and possibly a clay additive);
- a viscous but inert liquid, such as glycerin, is coated on the exposed paper to physically inhibit the leaching-out of salts as the developer is applied (Willis's 'glycerine development' method, see §3.3);
- substances are added to the sensitizer, such as salts of mercury(II) or lead(II), which enhance the reactivity of the platinum salts, but tend to change the image colour (Willis's 'Sepia Platinotype' papers, see §1.9).

Unreacted chemicals extracted into the wet development bath may also flow back into the paper and cause problems by reacting elsewhere to stain the high values, or 'bleed' at the edges of regions of high density. For a good quality of image, making the fullest use of the chemistry of the sensitizer, it is essential to ensure that there is sufficient water in the paper fibres either *before* or *after* exposure. This may be simply introduced from the vapour by hydrating the paper sheet in an atmosphere of controlled relative humidity.

If hydration is performed *before* exposure, then a substantial degree of print-out results, with several attendant advantages and characteristics:

- correct exposure can be found by inspection, without need of test-strips,
- the process is self-masking and so accommodates a wide range of exposure without 'blocking up' the shadow tones,
- negative contrast does not have to be controlled too precisely, because dense highlights can be 'printed down', accommodating a range of contrast in the negative which enables very delicate gradation in the high values,
- there is no need to impose a strict method of contrast control on the composition of the sensitizer, which is often deleterious to the image quality; for instance, the addition of potassium chlorate or dichromate to the platino-palladiotype can cause 'graining' and truncation of the tonal scale.

If vapour hydration is performed *after* exposure (but before wet-bath processing) and if the chemistry is sufficiently reactive, the image develops as the water vapour is absorbed, with the advantages of no diffusion, no loss or staining of the image, and smooth tones. The process may be continuously inspected, and the print 'pulled' when it has gone far enough. This is also what occurs in Herschel's 'breath-developed' processes.

The quantity of water present in the cellulose fibres will also have an important governing effect on the particle size of the image substance, which is a nanoparticle metal, and hence on the colour of the image. A large reservoir of fibre water will permit greater amounts of substances to react locally and therefore make it possible for the particles of metal to grow larger. Such particles will appear more neutral in hue. A very restricted pool of fibre water will constrain the print-out to producing small metal particles only, which can show quite marked colours – brown or sepia for silver and palladium, rather than black, and even pink, magenta and blue in the case of gold. Thus, regulating the hydration of the paper controls the colour of the image.

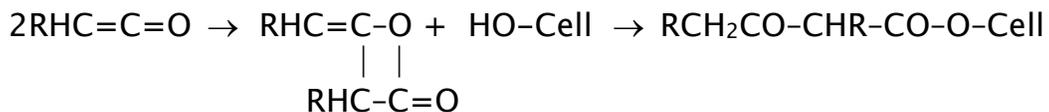
8.5 Criteria for siderotype papers

The best results with siderotype processes will be achieved on a high-quality cellulose paper, hand- or cylinder-mould made, having the following characteristics:

- **A pure, long fibre, α -cellulose furnish.** Purity and reproducibility in a paper are essential to the iron-based processes, so the only papers of serious interest to us are those made solely from cotton or linen, having a high (>98%) cellulose content. These are still sometimes called 'rag' papers, although recycled rags, once a major industry, are rarely used in their manufacture. For strength, it is desirable to select cotton with as long a fibre as possible, preferably of the type used for security papers. Papers made from a mixed furnish of cellulose fibres from different sources can absorb sensitizer unevenly, causing a fibrous granularity or blotchiness in the print, so should be avoided. Pure cellulose papers, carefully processed, have the best expectations of archival permanence of any substrate for printing.
- **A 'wove' mould rather than 'laid'.** Any watermark should be excludable from the picture area. Paper moulds are of two distinct kinds, depending on the pattern of interweaving of the metal wires: a 'wove' mould, with a structure like woven cloth, generally provides a more uniform paper texture which is preferable for pictorial purposes; a 'laid' mould of close parallel wires, bound by more widely spaced 'chain' lines, leaves ribbed lines visible as a watermark in the sheet, which is more suited for writing papers, unless it is particularly desired to give a strong sense of direction in the texture of the image.
- **A smooth, hot-pressed (HP) or cold-pressed (CP) surface.** 'Not' and 'Rough' surfaces may prove difficult to coat with sensitizer and may cause some loss of resolution in the contact printing. However, it should be noted that some heavily calendered, hot-pressed commercial papers do

not retain their smoothness on wet processing, which can cause them to swell and roughen perceptibly. Paper surfaces can be smoothed in the finished print by 'ferrotyping' against a metal plate, or pressing between perspex sheets in a letterpress.

- **Internal sizing with Alkyl Ketene Dimer (AKD).** Modern methods of internal sizing use reactive chemical agents called alkylketene dimers as additives to the pulp; one of the commercial substances has the trade name Aquapel™ – or other equivalent – and is the neutral sizing agent commonly employed by papermakers today. The molecule has a long saturated hydrocarbon chain, or 'tail' which is hydrophobic (repels water), and a 'head' consisting of a highly reactive functional group which can attach itself by bonding to the glycosidic hydroxyl functions (-OH) of the cellulose molecule. Thus water penetration is controlled by making the fibres somewhat hydrophobic. The advantage of internal or engine-sizing to the manufacturer is that no loft drying space is needed, as it is to 'cure' gelatin sized paper. If cellulose is simply represented by HO-Cell, the chemical reaction is:



alkylketene → alkylketene dimer + cellulose → cellulose alkyl β-keto ester
where alkyl = R = C₁₆H₃₃ (hexadecyl or cetyl).

- **A weight of ca. 160 g/m² (10 x 8 inches) to 360 g/m² (large sheets).** The thickness of paper is specified by its 'weight', expressed per unit area. The usual units are grams per square meter, abbreviated as gsm or, preferably, g/m². Some sources, especially in the USA, quote the weight of paper in the older measure of Imperial pounds (lbs) per ream; however this is meaningless unless the size of the sheet is also specified, and even the number of sheets per ream can vary in its definition. Application of a conversion formula is possible, if these extra data are known, to give an equation to convert weights in lbs to g/m². The relationship between the weight, G, in g/m² and the weight, W, in lbs (pounds) per ream is:

$$G = WF/AS$$

Where:

A is the area of one sheet in square inches

S is the number of sheets per ream (500 usually; can be 480 or 516)

F is a numerical factor converting the Imperial units to metric units.

For Imperial size (22 x 30 inches) sheets, we get the conversion factor:

$$G = 2.13 W$$

i.e. a '90 lbs' Imperial size paper is 2.13 x 90 = 192 g/m², etc.

- **No 'alkaline reserve' buffering agents such as calcium carbonate.** Calcium carbonate reacts with the sensitizer chemicals in an undesirable

way, precipitating insoluble calcium oxalate, (the same substance that causes some types of gall stone) and the liberated hydroxide ion tending to promote hydrolysis of the ammonium ferric oxalate, as described in Appendix IV. Pretreatment of a chalk-buffered paper with dilute acid (1–2% v/v hydrochloric acid or 5–10% w/v sulphamic acid for 10–20 minutes) will remove the chalk (the popular use of oxalic acid for this purpose is obviously chemically inappropriate because calcium oxalate is as insoluble as the calcium carbonate it is intended to remove).⁶³⁵ The quoted pH of the paper should preferably be less than 7, i.e. on the acidic side, so as not to promote hydrolysis of the applied iron sensitizer. This requirement runs contrary to the usual thinking on paper conservation, which favours the incorporation of buffers to prevent acidic embrittlement. However, with the present use it does not matter, from the conservation viewpoint, if the paper is fairly acidic initially, because in the course of wet processing it will be passed through baths that effectively de-acidify it and bring it to a favourable pH of 9 or so, before the print is finally dried.

- **No other additives** such as Optical Brightening Agents (OBAs) – fluorescent substances that make the paper appear extra-white, sometimes unnaturally so. Their archival stability has been questioned.. Wet strength agents inhibit disintegration of the wetted paper, and retention aids inhibit loss. Bleaches are used to decolorise delignified woodpulp – the so-called ‘woodfree’ papers – which are undesirable. Dyes or pigments stain the background, but may wash out. The greatest imponderable in plain paper printing is the effect on the reactive sensitizer chemicals of these paper-makers’ additives, which they are usually reluctant to disclose or discuss. Each commercial paper has its own idiosyncrasies, which may even vary from batch to batch or be changed by the manufacturer without notice. There is no substitute for personal trial and experiment. Once a satisfactory paper is discovered, it is wise to invest in a substantial amount of the same making.
- **Porosity or permeability to gases.** Since carbon dioxide is evolved during the exposure of siderotype sensitizers, the paper sheet must be sufficiently porous to allow this gas to diffuse through to the *verso* where it can then escape into the backing felts of the pressure frame, otherwise a bubble may form between the negative and the *recto* of the sheet, degrading the image resolution, as described in §7.20. Fillers such as china clay, giving the paper an extremely smooth and shiny look, tend to block the pores and diminish the porosity. Likewise, gelatin surface sizing may promote this kind of degradation.
- **Possible inclusion of biocides.** If it is possible for fungi or other micro-organisms to grow within stored paper sheets, they may influence the absorptivity of the paper locally and their colonies could cause the appearance of ‘blotchiness’ within a finished print. Such defects are

sometimes observed but their cause has not yet been proven; this is an issue requiring further research.

8.6 Conflicting standards of archival papers

Since the changes in industrial papermaking practice in the 1980s, it has become increasingly difficult to source paper suitable for coating with siderotype sensitizers. Paper chemist Dr. John C. Roberts of the University of Manchester Institute of Science and Technology summarises this historical shift in commercial practice as follows:

"For the period from around 1840 to the early 1970s paper was usually made in an acidic environment at pHs of around 4–5. This was because many grades required the use of rosin and aluminium sulfate for the control of water penetration (sizing), and solutions of aluminium sulfate exhibit a pH of around 4.5. Aluminium sulfate has also been popular with paper makers because it assists the flocculation of colloidal particles and therefore behaves as a mildly effective retention aid. However, since the early 1970s there has been a move away from acidic systems towards neutral and even slightly alkaline pH. The advantages of operating at higher pH are that there is reduced corrosion, greater strength arising from better swelling of fibres at higher pH, the possibility of using high filler additions and the energy savings associated with the easier drying of filled paper. This change has had a profound effect upon the whole of the chemistry of the aqueous fibre suspension."⁶³⁶

Increased awareness of the need for conservation of paper documents and works of art has led to the formulation by the International Standards Organization of specifications ISO 9706:1994 for Permanent Paper, and ISO 11108:1996 for Archival paper, whose content is summarised as follows:⁶³⁷

"Permanent paper (ISO 9706 : 1994)

shall have a pH value between 7.5 and 10.0
 shall have an alkali reserve at least corresponding to 0.4 moles acid [H⁺] per kilogram of paper (corresponding to at least 2% w/w calcium carbonate)
 shall have tearing resistance of at least 350 mN
 shall have a Kappa number less than 5, which means that the paper may contain only a small amount of easily oxidized material (e.g. lignin).

Archival paper (ISO 11108 : 1996)

shall be made from cotton, cotton linters, hemp or flax, but may contain a minor fraction of fully bleached chemical wood pulp
 shall have a folding endurance of at least 2.18 (MIT-, Köhler Molin- or Lhomargy-instruments) or 2.42 (Schopper instrument)
 Archival paper shall meet the requirements for permanent paper.
 The archival paper is stronger than the permanent paper and can withstand considerably more handling."

From these specifications, we may calculate the implications of the presence of this equivalence of 0.4 moles of base per kilogram of paper, which implies an [OH⁻] equivalent volume concentration of ca. 0.3 molar in the paper:

If the paper weight is, say, 250 g/m², then a 1 m² sheet contains:

$0.25 \times 0.4 = 0.1$ moles of OH⁻ equivalent.

A typical coating volume of siderotype sensitizer would be 25 cm³/m² of a solution ca. 0.5 molar in Fe(III)

i.e. a 1 m² sheet of paper would absorb 0.0125 moles of Fe(III) on coating.

It follows that, per unit area, the permanent and archival papers contain an 8-fold molar excess of alkaline reserve (equivalent to [OH]⁻) available to react with and hydrolyse the Fe(III). There is clearly great potential for damage to the sensitizer chemistry if only a fraction of the alkali in the sheet can contact the iron(III) salt, area for area, in the wet state, although the chalk buffer is quite involatile and unlikely to migrate through dry paper.

This accounts quantitatively for the fact that, over the last few decades, it has become increasingly difficult to find papers which work well for platinum-palladium printing, among the high quality cotton papers manufactured for the fine-art market of watercolorists, sketchers and printmakers and the archival document market, which all presumably conform to the above ISO standards. Such papers now always boast that they are "acid free" – implying that they probably contain an additive of chalk filler which, unfortunately, will rapidly cause the decomposition of any iron(III) sensitizer. Most contemporary Pt/Pd practitioners have been driven to the last resort of soaking their chalk-buffered papers in dilute acid in order to destroy the calcium carbonate before coating them with sensitizer. Unfortunately many practitioners think that oxalic acid is suitable for this purpose, but calcium oxalate is even more insoluble than calcium carbonate, and will precipitate out (§7.6). Hydrochloric acid, 5% v/v (ca. 0.6 molar), can be used to decalcify the paper, but recently Sirdar Bilici has found it very convenient and effective to employ a bath of 10% sulphamic acid for 20 minutes for this purpose, followed by an hour's wash.⁶³⁸ Nonetheless, it is a tedious and unnecessary procedure that tends to degrade the paper surface and strength.

The only complete answer to the problems posed by present-day high quality commercial papers, is to enable the siderotype printer to gain some control over the paper specification, by commissioning a special paper to be made by hand. Fortunately there still remain a few artisans who have kept alive the skills of hand-making paper, and it is only through the willing and patient cooperation of one of these craftsmen, that the following initiative became possible.

8.7 Handmade paper for siderotypes

The author has been personally associated with a 100% cotton handmade paper called 'Buxton' paper, first developed in 1993 by Ruscombe Mill in Gloucestershire, to possess all the characteristics that have been specified above in §8.5 for alternative printing in the iron-based processes.⁶³⁹ The development of this paper arose originally from a collaboration between the author and Chris Bingham, master papermaker of Ruscombe Mill. The name that Chris chose for it – *Buxton* paper – was a nice reference to the author's home town, which has been noted historically from Roman times for its spa waters, as *Aquae Arnemetiae*. The evolution of Buxton paper has called for several trial

makings, in response to initial specifications that were drawn up in 1992, testing the product each time by alternative photographic printing, and then much frank discussion and negotiation to solve any contingent problems. In the late 1990s, Ruscombe Mill was relocated to Margaux in France, in the heart of the Haut Médoc, where it shares the excellent local water with the winemakers. Buxton paper continues to be made there, on demand, and a gelatin-sized version of the 240 g/m² sheet, called 'Talbot' paper, was also tested. Like the superb vintages from the celebrated chateaux that surround it, Ruscombe Mill at Margaux produced the *grand cru* of fine-art papers.⁶⁴⁰

Buxton paper is not made from the linters of the cotton plant, but from finest quality long cotton fibre, nearly 100% α -cellulose, which is stronger and has a natural white colour. The paper has been cold-pressed, leaving an attractive 'tooth' to give life to the surface, which does not change significantly after wet processing. It may be further ferrotyped or calendered in a press, which improves the ease of coating. The pH is approximately 7.5, very close to neutrality, without additives. Buxton paper is currently available in Imperial sheet size (22 x 30 inches or 56 x 76 cm) with four deckle edges, of course since it is handmade, of weights either 160 g/m², or 240 g/m².

Being hand-made, Buxton paper has no preferred machine direction, *i.e.* the fibres are randomly oriented. It is therefore equally strong in all directions and dries flat without curling. The dimensional stability is high: its size changes by less than 0.5% after a first cycle of wet processing and drying, making it suitable for multiple printing, where accurate re-registration of the image is paramount. The attractive texture of the surface may also commend it as a substrate for gum dichromate, and the other alternative printing processes employing a layer of photohardened colloid. Because it is hand-made, users should not expect the sheet to have quite as high a uniformity as a machine-made product. Its individuality should be a source of pleasure to the experienced maker of handcrafted prints; it is not a beginners' paper.

8.8 Furnishings of flax versus cotton

Problems with the quality of cotton furnishings supply in 2011 eventually caused Chris Bingham, the master papermaker at Ruscombe Mill to develop a new paper which differs from all other alternative process papers in being handmade from 100% linen cellulose fibre (*i.e.* made entirely from the best quality flax, not cotton): he has decided to name it 'Herschel' paper.

Linen is a 'bast fibre' from the stem of the Common Flax plant, *Linum usitatissimum*. Its fibre has a similar size to cotton, §8.1, but is cylindrical with a thick cell wall and a lumen of relatively small diameter. It has periodic knots or nodules, resembling bamboo. When beaten it fibrillates more extensively than cotton, so forms a stronger, less elastic paper sheet (figure 8.5).

It is possible – but not yet proved scientifically (by electron microscopy) – that the different performance of flax versus cotton cellulose for siderotype lies in the fibre morphology constraining the image substance (see Fig. 8.4 and 8.5). The structure of the flax fibre may enhance its ability to retain nanoparticles of image pigment, which is essential to the success of all siderotype processes.



Fig. 8.5 Flax fibres

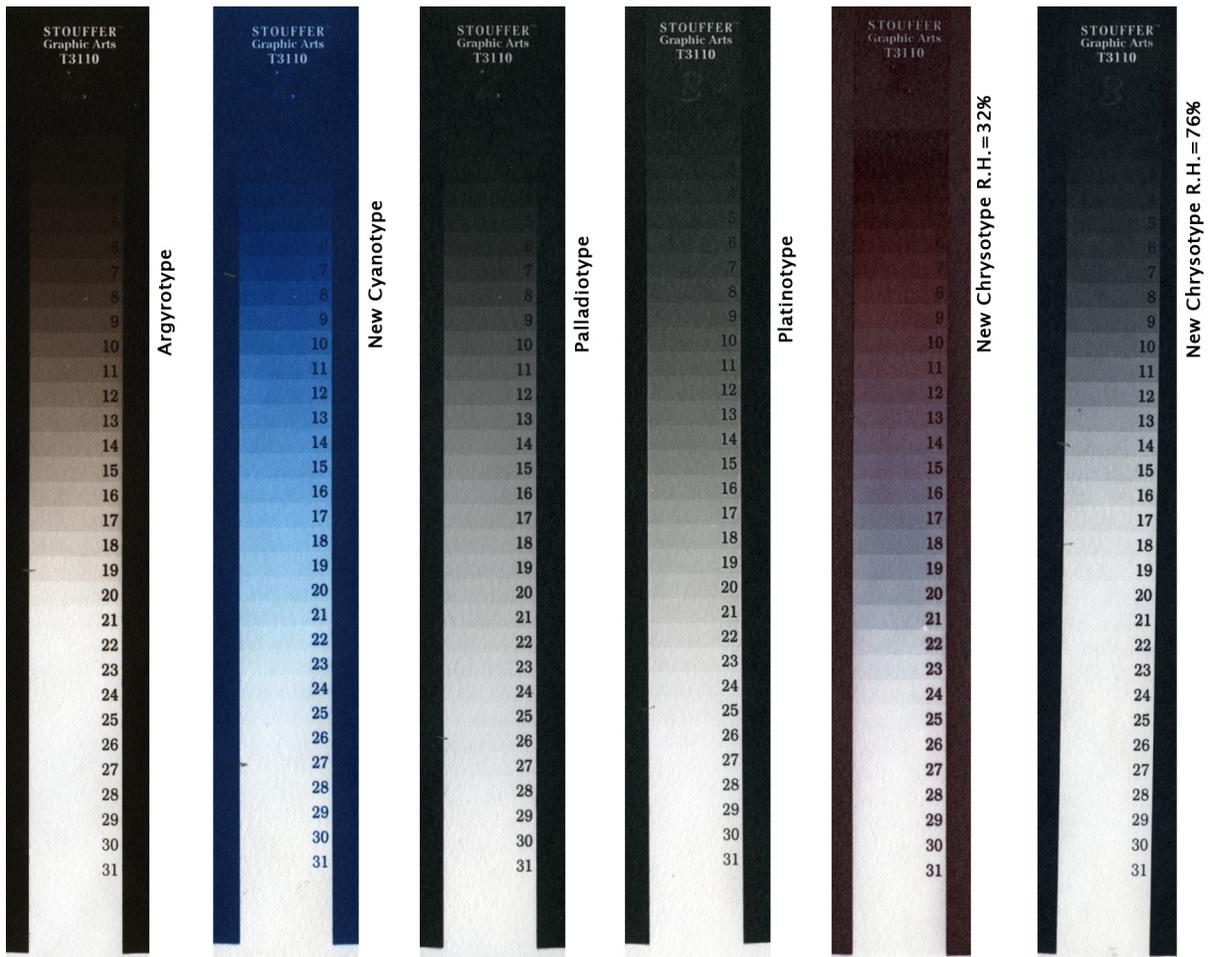
Herschel paper, like Buxton, is 'engine-sized' with neutral alkylketene dimer, AKD. It can be rod-coated with sensitizer solution similarly to Buxton, with the addition of Tween 20 surfactant to the sensitizer, to ca. 0.1–0.2%. There is, of course, absolutely no added chalk buffer in this paper, which seriously inhibits siderotype, no surface sizing such as gelatin, which 'kills' platinum, nor clay or gypsum fillers, optical brightening agents (OBAs), etc. With all processes, the D_{\max} is high, the cold-pressed surface is perfectly matte with a fine tooth texture, the clearing of whites in the wet processing is rapid and complete, and the gradation and smoothness of the image tones are excellent. This linen paper sheet has much greater resilience and wet strength than cotton papers, notwithstanding its moderate weight of 200 gsm. Dimensional stability is good, with about $\pm 1\%$ hydroexpansivity; but to obtain a perfectly flat sheet after processing, it does need to be dried carefully under some pressure.

Tests of Herschel paper with argyrotypes, new cyanotypes, palladiotypes, platinotypes and new chrysotypes (see Fig. 8.6) show that it performs superbly with all these processes – better even than Buxton paper in some respects.

During the wet processing, there is no bleeding of image substance – even Prussian blue, which is notorious. The colour of the silver images it yields with the argyrotypes process is particularly satisfying, as is the range of colours obtainable with new chrysotypes, which are also dependent on particle size.

'Herschel' paper will prove an excellent replacement for Buxton, with the advantage that the Mill's supply of linen cellulose fibre (from flax grown in Northern France or Belgium) is more reliable and consistent than present supplies of cotton. In high quality papermaking, confidence in the raw materials

is paramount. One need have little worry about archivality, because linen was the first plant fibre historically available to Europeans for making fabrics. Long before the growth of the cotton textile industry towards the end of the 18th century, linen rags were being processed in the 15th century for European papermaking, and such papers have endured well to this day. Linen security papers have also been used in modern times for banknotes, bonds, and other precious documents.



Siderotype Tests on Ruscombe Mill's 'Herschel' Paper – 100% Linen. Stouffer T3110 Step Tablets. Mike Ware 2011

Fig. 8.6 Siderotype tests on 'Herschel' linen paper.

8.9 Handling of "vellums"

The original meaning of "vellum" was a parchment made from the bleached and scraped skin of a calf (Old French: "vélin" = calfskin), but the use of the term "vellum" in modern papermaking denotes a sheet quite different in origin, and entirely vegetable: the cellulose paper pulp is heavily beaten to produce a translucent or even semi-transparent sheet: "tracing paper". The following advice comes directly from Pradip Malde's account of his personal practice with one such paper:⁶⁴¹

"The specific name of the paper is Wyndstone Vellum #165243, and my preferred weight is 5pt. Manufactured in Germany, and imported into the USA with this name, the paper is 'naturally' translucent, as opposed to the more common practise of chemical transparentizing used in the manufacture of most vellums. It has been sized for the reprographic/printing industry, and is slightly acidic. The paper has been manufactured with totally chlorine-free water. The furnish is wood cellulose, using a mixture of hard and soft woods, including some eucalyptus, but the US distributor (Sam Flax in Atlanta, Georgia) insists that the paper is lignin free.

Surfaces

Using this paper is not for the faint of heart. While it may be hardly apparent when looking at the dry, uncoated paper, there is a wire and a felt side that will show up once the print is dry. It is difficult to determine which side is which with the naked eye. When cutting down the full sheet, stack all paper with the same side up. Thus, once you make a first print from the stack, it will be possible to identify surfaces by the way the stack lies. Another, more subtle indicator comes from the curl of the paper: the convex side is the felt surface.

Coating

To coat a 8x10 inch area, 1.3 cc of sensitizer solution is ideal, allowing for 5 passes with a coating rod. The paper is less absorbant than other papers. Consequently, you may feel as though embarking on a fifth pass is risky. Having said that, I have given this paper as many as 6 passes without any deterioration. It is essential that the paper is taped down onto glass, parallel to the grain or fiber direction. If using a glass coating rod, which I recommend, then the passes should be made perpendicular to the grain. This will render smoother passes. Once damp, the paper tends to curl dramatically. A simple method of preventing unmanageable curling from this point on through to drying is by attaching two clothes pegs to the lower end of the paper. The pegs themselves are attached to a 'cross-piece' of 3/16" dowel or plexiglass tube. This structure tends to hold the paper relatively flat during drying. A similar arrangement can be used for the top end of the paper too.

Drying

Drying times are as normal for other papers (10 minutes at around 40°C)

Assessing exposure

(this applies to printing-out processes such as the Ammonium Pt-Pd system, Chrysotype and the New Cyanotype)

During exposure, have a piece of white paper or thin white card handy as you prepare to inspect. Slipping it between the coated paper and the negative will make assessment easier. I have also found that it helps to place the contact printing frame face down on a white surface – as I swing the back open and lift the negative, the image projecting through the translucent paper gives me enough information to make a fairly accurate estimate of exposure. At full print-out, highlight values (zones VII – VIII) are still difficult to see, They will only become apparent once the paper is dry and sitting on an opaque white surface.

Processing

The paper is very robust and has good wet strength, but it is tremendous dimensional expansion. It tends to kink easily, therefore handle it with about the same care as with papers lighter than about 160 gsm. Process normally, finishing with a 30 minute wash in a very gentle flow of water.

Drying

Drip dry by placing the washed print on a vertical sheet of plexiglass/ perspex or glass. Once all surface water has drained (about 15m), place face up on a screen. Be warned and do not panic: the paper will go through buckling contortions of geological proportions. Once dry, it will like dried seaweed, but somewhat flatter. At this point, press the print under some weights for a couple of days, or better, between two preheated sheets of matt board in a dry mounting press at around 70 C/160 F for about 60 seconds.

Calendering

The print can be given a very slightly finer surface by a process of 'pseudo-calendering'. After it has washed and drained, place it face down on a very clean sheet of plexiglass, cover with three or four layers of blotting paper, and apply a roller over the entire print with considerable pressure. Uncover and peel off gently. This can be better accomplished if you have access to an etching press.

Mounting/Matting

Vellum, being highly dimensionally unstable, can begin to buckle in humid environments. For exhibitions, it is best to matt, frame and display these prints in an atmosphere of less than 60% RH at around 20 C. This means that frames should be sealed. An alternative is to dry-mount the paper onto archival board, using archival dry-mounting tissue (I recommend Seal MT 5 or Seal Buffer Mount.) As with any material behind the print, the color of the tissue will affect the print color due to the vellum's translucency."

8.10 Machine-made papers for siderotypes

From time to time a few papermaking mills, operating on the industrial scale with mould or Fourdrinier machines and super-calenders, have been persuaded to take on the needs of the alternative process constituency, see §4.2, although in terms of quantity this is a niche market, requiring for its siderotypes different criteria from the usual fine art paper market (§8.7), and it has been a difficult task persuading the papermakers not to include any chalk in their furnishings. Among the unbuffered papers machine-made specifically for alternative processes are Cranes Platinotype (now discontinued), Arches Platine,⁶⁴² Bergger COT320, Weston Diploma Parchment, Magnani Revere Platinum, and most recently Hahnemühle Platinum Rag.⁶⁴³ This last-named paper has been tested using the 'traditional' palladium, and platinum-palladium development processes, and found to perform very well, and perhaps the best of all. Using a conventional ferric oxalate/sodium chloropalladite sensitizer at 75% RH, the master printer, Stan Klimek, reports:

"...processed with Potassium oxalate room temp. cleared. Dmax - 1.42 and a log of 2.5. The paper was very easy to coat, smooth and even and cleared easily with a 5 minute bath of water before clearing agents. Very smooth transition of tones as can be viewed 21 step. In addition (not shown here

was a step-wedge test with ammonium citrate which yielded equal response with the potassium oxalate and a very neutral black which is so hard to get from all other papers I have used...

This is a wonderful paper with no quirks, Hahnemuhle has done an excellent job in engineering from the ground up a paper that was tailored for the alt processes."

Many other noted practitioners, such as Keith Schreiber, have echoed his findings, also using the paper successfully with mixed platinum-palladium and even pure platinum sensitizers.⁶⁴⁴

8.11 Japanese handmade papers: "washi"

The traditional handmade papers of Japan, which are collectively known as "washi", have occupied a central place in Japanese culture, art, and calligraphy for well over a millennium; but they are very different from the products of Western papermaking. The finest washi are prepared from pulps consisting of fibres derived from the stripped bark of various indigenous deciduous shrubs: "kozo" (mulberry, *Broussonetia papyrifera*), "mitsumata" (*Edgeworthia chrysantha*), and "gampi" (wild shrubs of the genus *Wikstroemia*).

Around 1910, washi was employed for platinum printing by some members of the Photo-secession in the USA: notably, Frank Eugene and Gertrude Käsebier, who exhibited such prints in Buffalo; Stieglitz's publication *Camera Work* also contained some photogravures on washi.

In recent years, with the renaissance of platinum-palladium printing and its spread to Japan, a few workers have once again taken up the challenge of printing on washi. This interest has brought a positive response from the Japanese paper-makers themselves: in the prefecture of Kochi, a leading region for the production of Tosa washi, a project was initiated in 2011 to discover and develop the best kind of washi for platinum-palladium printing. By 2013 the Japanese Paper Museum of Ino town was able to hold an exhibition displaying the outcome of their research. The progress of this project and its findings are reported in Japanese and English in the book: *Creating New Value with Tosa Washi: Platinum & Alternative Photo Processes*,⁶⁴⁵ which also displays the work of several artists in the medium. After numerous test-makings and printings, a mixture of kozo and gampi in the proportions of 80% to 20%, respectively, without the use of any sizing agent, was settled on as the furnish for the washi, which is called Tosa hakkinshi; its weight is 28 gsm. It is now widely used by platinum-palladium printers favouring this medium.⁶⁴⁶

In the neighbouring prefecture of Tokushima, a similar paper called Awa washi is manufactured by the Awagami Factory group using chiefly kozo, mixed with some mitsumata. Their website provides quite extensive information on washi and its history.⁶⁴⁷ Awagami has recently marketed both gampi and mitsumata washi, specifically intended for platinum-palladium printing.⁶⁴⁸

In 2012 the leading fine art publisher, Amana Holdings of Japan, entered a partnership venture with Salto Ulbeek of Belgium, noted for their high-precision digital printing technology, to found the joint corporation called Amanasalto. This established an advanced platinum-palladium printing studio in Tokyo, and acts as agent for 'high end' portfolios of platinum-palladium work by a number

of celebrated artists.⁶⁴⁹ In 2013 Amanasalto published an elegant promotional catalogue volume entitled *Introduction of Platinum prints*.⁶⁵⁰

A washi sheet tends to be very light in weight – 20 to 30 gsm is typical – which naturally makes handling the fragile prints during wet-processing quite difficult, demanding considerable skill in their manipulation. However, a number of advantages can be claimed for washi: there is usually no sizing, and no chalk alkaline buffer is used; the paper has a neutral pH 6.5–7.5, and it contains about 1/10th the amount of cellulose as a typical Western paper sheet, so there is much less cellulose available to absorb and trap contaminants such as iron(III), and clearing procedures can adopt a ‘lighter touch’. Moreover, it is reported by users that the D_{\max} achievable on gampi and kozo can reach upwards of 1.7–1.8, a whole stop superior to the D_{\max} of approximately 1.40–1.45 using a typical Western paper.⁶⁵¹ This is a remarkable observation, considering the thinness of the sheet, and must be a consequence of the absence of any sizing in these papers allowing a greater metal concentration in the surface layer of the image, thus generating a higher optical density in diffuse reflectance than is achievable in sized Western papers – see §8.3.

In its lightest weights, ca. 10 gsm, washi is quite translucent – almost transparent; one such paper, a 100% gampi, has been successfully employed by photographer and printmaker Gilles Lorin to make palladium prints with a backing of reflective gold leaf to provide strikingly luminous images, that Lorin has named “orotypes”; examples may be seen on his website.⁶⁵² These are the palladium equivalent of the earlier “orotones” of Edward Curtis, ca. 1900, in which a toned silver-gelatin diapositive on a glass plate was backed with gold leaf or paint.⁶⁵³ The lightest weight of washi calls for scrupulous care in the processing baths and minimising reagent strength; alkaline tetrasodium EDTA tends to cause damage to the fibres, so the use of mildly acidic diammonium citrate as developer and clearing agent is preferred. I thank Gilles Lorin for generously communicating his findings and details of his working practice. Platinum-palladium prints on vellum (§8.9) have also been similarly backed with gold leaf by Dan Burkholder in 2007.⁶⁵⁴

9. Deterioration and Post-Treatment of Platinum Prints

In his *History and Practice of Platinum Printing*, Luis Nadeau makes a wise observation, reminiscent of Stieglitz's condemnation of "sloppiness" (§3.2):

"Platinum workers tend to be careless because they wrongly believe that platinotypes are permanent no matter how they are processed."⁶⁵⁵

While it is true that there is no substance that can reasonably be encountered in a normal environment with the ability to attack and diminish the platinum image, this fact does not guarantee total immunity for the finished Platinotype, which can suffer deterioration in a number of other ways: some of them a consequence of improper processing leaving residual substances, some due to the deliberate presence of other metals such as mercury or lead, and some a result of that unavoidable Achilles' heel – the high catalytic activity of platinum.

9.1 Staining of Platinotypes by sulphides

Almost as soon as Platinotypes became widely known, their permanence was called into question. In 1880, van Monckhoven treated specimens with hydrogen sulphide gas and complained that this caused a yellowing of the high values.⁶⁵⁶ In February of the same year John Spiller subjected Platinotypes to a whole barrage of destructive tests, including strong acids that would obliterate any silver print, but found only one substance that caused any deterioration at all, ammonium sulphide, which dulled the highlights.⁶⁵⁷ These yellow discolorations caused by sulphides were attributed to the presence of the lead(II) and/or silver(I) salts that Willis employed in his early sensitizers. (Although lead sulphide, PbS, and silver sulphide, Ag₂S, appear black in bulk, absorbing light across the entire visible spectrum, when the particle size is small the absorption edge moves towards the blue, causing a colour shift to yellow.) The dark sulphides are also fairly easy to oxidise to colourless substances when the stain is removed by "chloride of lime". This unfavourable observation provided an incentive, spurring Willis on to eliminate both metals from his newly-formulated papers of 1880, which were tested by George Dawson and found to be unaffected by ammonium sulphide.⁶⁵⁸

The issue then subsided while Willis's papers presumably remained lead-free until it was rekindled in 1887, when Andrew Pringle (§1.7) published his observation of the yellowing of Platinotypes by hydrogen sulphide solution.⁶⁵⁹ By this time, Willis's patents (Appendix VIII) reveal that he had recently been obliged, in the interests of image quality, to re-introduce either lead or mercury salts into his sensitizers. This defect was immediately seized upon as revealing a vulnerability of the process, especially by the ardent proponents of silver printing who resented Platinotype's claim to superior permanence and therefore sought to undermine it. An energetic correspondence ensued in the early issues of the *British Journal of Photography* of 1887, which grew at times quite acrimonious, with strong defences being put up by Herbert B. Berkeley, a partner in the Platinotype Company.⁶⁶⁰

On the contrary side of the argument, Pringle's observation of the "sulphuration of platinotypes" was confirmed by others such as H.H. O'Farrell,⁶⁶¹ and the problem of yellow discoloration in Platinotypes was recognised and explicitly discussed in 1887 by Henry Chapman Jones (1855–1932), a chemist at the Royal College of Science, London.⁶⁶² However, he attributed the staining mainly to the presence of iron in the paper. In 1895 he described further experiments to demonstrate that, even after immersion for four hours in dilute hydrochloric acid, unexposed Platinotype paper still retained some residual iron, detectable by discoloration under the action of hydrogen sulphide.⁶⁶³ Chapman Jones also noted that in processed Platinotypes he found more iron in the darker parts of the image than in the lighter – an observation of relevance to the action of Packham's Toner that follows below in §9.3.⁶⁶⁴ Platinotype practitioners of the time seem to have paid little heed to his warnings: Chapman Jones's early demonstration of the presence of iron, even in Platinotypes thoroughly cleared in hydrochloric acid, has been largely forgotten until the present time.

9.2 *Slow development of iron stains*

Quite distinct from the yellow stain caused by the deliberate application of sulphides, an insidious slow development of yellow stain seems to have been endemic to the Platinotype process throughout its history. But this stain could not have been immediately conspicuous on making the platinotypes, otherwise the practitioner would have rejected them, or more likely persisted with a clearing treatment until stain was no longer evident. However, the cut sheets of commercial Platinotype papers of those times were invariably sensitized to their very edges, and the images were usually printed without masked borders; there were therefore no clear margins of uncoated, or coated but unexposed, paper left for comparison, to check the effectiveness of the print clearing procedure, as described in §7.22 and §10.10.

To remove excess iron and platinum salts from Platinotypes, it was generally recommended that they be cleared for five to ten minutes in each of three successive baths of hydrochloric acid, diluted 1:60 from concentrated (36% *w/w* HCl) acid, followed by thorough washing, for as much as two hours.⁶⁶⁵ Palladiotypes, however, cannot be treated so brutally without incurring intolerable image loss (see §2.7): the necessity to employ more dilute (1:200) hydrochloric acid in their processing provides one reason for their being less well cleared of iron salts, and therefore even *more* susceptible to yellowing than Platinotypes.

That yellow staining may take months or even years to become manifest in Platinotypes and Palladiotypes, where none was apparent immediately following the original processing, must be attributed to the slowness of the chemical reactions causing this intensification of colour, which calls for a chemical explanation that will be considered in §10.2 and §10.8.

9.3 *Packham's catechu toner*

Packham's method for toning Platinotypes brown, which was first published in 1895, is also relevant to the issue of iron stains in Platinotypes.⁶⁶⁶ The toning

agent, catechu (or "cutch"), was obtained from an aqueous extract of Acacia wood, and had long been used as a brown dyestuff for textiles, as mentioned above. James Packham employed a hot, very dilute alcoholic solution of it to tone fully processed black Platinotypes into images of various shades of brown, with a density proportional to the platinum deposit; *i.e.* it was not simply a dyeing or staining of the paper base. As his explanation for the toning action, Packham laboured under the misapprehension that:

"catechu possesses the property of combining with platinum under certain conditions".

Packham held to this view despite his own observation of the likely cause:

"...he could not get the colour without the iron, and when the iron was present he invariably got the colour... The more iron left in the print the greater was the change of colour produced by toning, but it was obvious that if too much iron remained there must be a fogging effect in the highlights."⁶⁶⁷

"Development appears to have a decided effect in governing the after-colour of all kinds of platinum prints. Old baths of the potassium oxalate that have been repeatedly employed give the prints an increased affinity for the colouring matter."

But Chapman Jones immediately recognised and put forward the correct explanation in 1895,⁶⁶⁸ namely that the residual iron(III) salts in the print act as a mordant for the catechu, reacting with it to give a deep brown dyestuff:

"The author has shown that this toning is due to the action of the extract upon the iron compound left in the print, which it is exceedingly difficult if not impossible to remove completely, and that other substances that give intense colours with iron salts would give similar results, though perhaps not such desirable colours. The fact that the image is toned appears to be due to the fact that the platinum holds the minute residue of iron more tenaciously than the paper alone, and that the residual iron compound is therefore roughly proportional to the depth of the platinum deposit."⁶⁶⁹

The principal component of catechu is a flavonoid polyphenol, *Catechin* C₁₅H₁₄O₆: 2-(3,4-dihydroxyphenyl)-3,4-dihydro-2H-chromene-3,5,7-triol. See fig.9.1. Catechin is colourless and crystalline when pure, and soluble in hot water and alcohol. Like other catechols, it coordinates with iron(III) in basic solution, to form a dark reddish-brown tris-complex [FeCat₃]³⁻. Similar reactions are seen in the formation of highly coloured complexes of iron in the iron-gall ink used for manuscript writing since mediaeval times, and in the "black whisky" beloved of some Glaswegian drinkers,⁶⁷⁰ where the tannins imparted to the spirit by maturing in oak-casks react with iron(III) in the added water from a local chalybeate well.⁶ Catechin is also crucial for the flavour of

⁶ *Etymological footnote 6: The adjective 'chalybeate' derives from the tribe of Chalybes, metallurgists of Anatolia, living on the east coast of the Black Sea, who are credited with the first extraction of metallic iron from its ores, some time around 1500 BCE.*

cider,⁶⁷¹ and occurs as a gallate ester in red wines and green tea, and is believed to be beneficial: truly, a drinker's molecule!⁶⁷²

The significance of this to the present study is that the action of Packham's Toner is consistent with Chapman Jones' little-known finding that there is *more* residual iron in the shadow tones than in the highlights of a Platinotype. The chemical reasons for this, and its implications are considered later in §10.8.

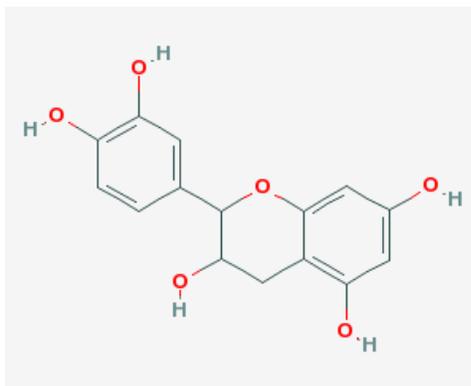


Fig. 9.1 *The structure of catechin*

9.4 Early treatments for iron stains

Treatments for yellowed Platinotypes were commonly advised in the early 20th century photographic literature:⁶⁷³ all followed Chapman Jones's original recommendation⁶⁷⁴ of immersion in sodium or calcium hypochlorite bleach solution plus a little hydrochloric acid, to liberate chlorine.⁶⁷⁵ This was of questionable value in the long term, because the stain often returned, and the reagent was damaging to the paper strength. The deleterious and rather ineffectual nature of all these early treatments with hypochlorites have been reviewed in some detail by photograph conservator, Erin Murphy.⁶⁷⁶ The same treatment cannot be applied at all to Palladiotypes because such a chlorinating bleach rapidly dissolves palladium metal and destroys the image. These early procedures have already been reviewed and tested on Palladiotype and Platinotype simulacra by Constance McCabe, and rejected as possible conservation procedures for Palladiotype.⁶⁷⁷

A similar bleaching agent which later found some recommendation for removing iron stains was chloramine T. This is the sodium salt of *N*-chloro-4-methylbenzenesulphonamide, widely used as a mild biocide:

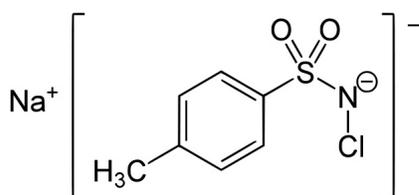


Fig. 9.2 *The structure of chloramine T*

It tends to release hypochlorite ions in solution, so has also been commonly employed to remove iron stains from paper artefacts, and was used

by pioneer photograph conservator Jose Orraca at George Eastman House to treat some of the 48 platinum prints by Peter Henry Emerson in the so-named *Cuba Album*, donated by his nephew, because it includes views of Cuba as well as the Norfolk Broads. The history of its conservation treatments has been fully documented by Gary Albright, and further involves the use of a solution of chlorine dioxide by Alice Swann.⁶⁷⁸ However, as reported by Robert Aitchison, chloramine T has also been found to dissolve palladium by oxidising the metal, so it is quite unusable as a conservation treatment for prints containing this metal.⁶⁷⁹

More recently the conservation treatment of iron-gall ink documents has recommended stabilization, rather than removal, of the iron as a preferred procedure. This can be achieved by treatment with sodium phytate (inositol hexakisphosphate), Fig. 9.3.⁶⁸⁰

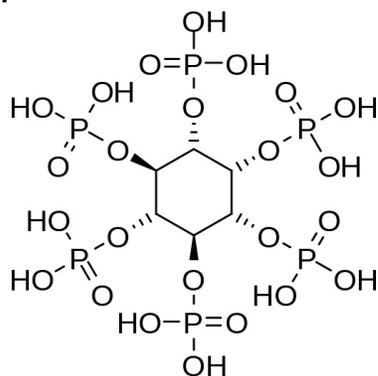


Fig 9.3 The structure of phytic acid

This procedure renders the iron inactive towards the Fenton reaction (§10.4). While it also suppresses the yellow discoloration, because iron(III) phytate is colorless, it does not actually remove all the iron, because iron(III) phytate is not very soluble. This treatment is therefore deemed inappropriate to the problems presented by Platinotypes, and has not been pursued at this time.

9.5 Artificial generation of iron stains

An important objective of present research ought to be to identify unequivocally the chemical nature of the yellow stain that is generated naturally in many Platinotypes, (rather than that which is caused by the treatment with sulphides, §9.1). While it is usually presumed to be due to the presence of residual iron(III) compounds, see §10.2, its exact chemical nature has not yet been confirmed. Suitable techniques that could be applied to characterise the chromophore include UV-visible spectrometry, infrared and Raman spectroscopy, electron paramagnetic resonance, and magnetic susceptibility measurements.

The yellow stain could also have contributions from residual salts of platinum or palladium, or from chromophoric groups formed in oxidised cellulosic species – so-called 'oxycellulose'; these are possibilities that need, at least, to be considered and eliminated.⁶⁸¹ Furthermore, the nature of the staining substance may differ between the highlights of the print, where it is obvious, and the shadows where it is invisible (see §10.7) unless, with the

elapse of time, it diffuses out, producing a halo-like stain around the dark area – a phenomenon that has been observed in some historic prints.

In an attempt to reproduce, under controlled conditions, the discoloration of historic Palladiotypes (§3.8) and Platinotypes, experiments were carried out at the NGA by accelerated ageing of simulacra (§6) in a humidity-controlled oven. The parameters initially chosen for this treatment were: an elevated temperature of 70°C, an RH of 75%, and a dark environment, which seems more appropriate to the conditions of storage. The duration of exposure to these conditions was four weeks (672 hours). The ageing of the samples was followed by colorimetry (CIE L*a*b* units) and XRF spectrometry.⁶⁸²

The final results depended on the processing procedures. Matthew Clarke and Dana Hemmenway analysed the residual iron content resulting from platinum and palladium printing tests with various wet bath processing times (multiples of 10 minutes to one minute) which ranged from ‘well-processed’ to ‘poorly-processed’ and were carried out by: long clear and long wash; long clear and short wash; short clear and long wash; and short clear and short wash. In the worst category of processing ‘short cuts’ the residual iron concentrations were significantly raised, and more so for palladium than platinum prints. Although all the specimens showed little or no visible iron stain immediately after preparation and would have been judged acceptable as artists’ prints, the artificial ageing of such specimens caused the appearance of yellow stains that correlated with the concentration of residual iron measured by XRF. The stain was progressively worse in the ‘poorly-processed’ specimens. It was also shown that the occurrence of stain did not depend on the presence of platinum salts: a sensitizer of ferric oxalate alone gave similar results. However, papers sized with gelatin were found to retain more iron than those sized by alum/rosin. The yellowish-brown stain measured by colorimetry was seen to be very similar to that occurring in some historical specimens of platinotype.

9.6 Conservation treatments for iron stains

The removal of iron stains from paper objects has long been a standard treatment procedure used by leading professional conservators of works of art on paper, such as Aitchison and Watters, Inc. A method of reductive dissolution of proven value is provided by treatment with sodium metabisulphite (now called sodium disulphite), Na₂S₂O₅. Disulphite anion reacts with water to give the hydrogen sulphite anion:



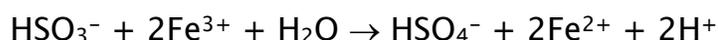
which has the following redox potentials in acid and alkali, respectively:

$$E^\ominus(2\text{SO}_4^{2-}, 2\text{H}^+/\text{H}_2\text{SO}_3) = +0.17 \text{ V}$$

$$E^\ominus_{\text{B}}(\text{SO}_4^{2-}/\text{SO}_3^{2-}, 2\text{OH}^-) = -0.93 \text{ V}$$

The method involves treatment first with 4% sodium disulphite solution which reduces the iron(III) to iron(II):

$$E^\ominus(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.771 \text{ V}$$

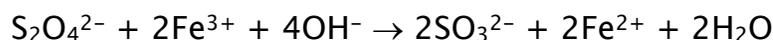


This is then followed by washing and then treating with dilute (1.5% v/v) hydrofluoric acid to solubilise and remove iron(II) as the complex fluoro-anion $[\text{FeF}_6]^{4-}$.⁶⁸³ This procedure is chemically sound and effective for platinum and platinum-palladium prints; appropriate precautions are required for the safe handling of hydrofluoric acid.

In recent times, safer and more effective treatments have become possible with chelating agents such as EDTA (ethylenediaminetetraacetic acid), see §10.9, first available in the 1930s. However, it appears that effective removal of Fe(III) from cellulose cannot be accomplished by chelating agents alone: recent measurements have shown that only 50% of the Fe(III) is removed from suspensions of cellulose pulp, even by powerful chelating ligands such as CDTA (cyclohexanediaminetetraacetic acid) and DTPA (diethylenetriaminepentaacetic acid), see §10.9.⁶⁸⁴ More complete removal of iron requires *reductive* dissolution as described above: by initial reduction of Fe(III) to Fe(II) the binding energy to cellulose is diminished, and the chemisorbed Fe(II) is then easier to detach and solubilise with appropriate ligands. Sodium dithionite, $\text{Na}_2\text{S}_2\text{O}_4$, is favoured as the reductant in modern conservation treatments;⁶⁸⁵ this is a more powerful reducing agent than disulphite, described above, and more effective in alkaline solution than in acid, as can be seen from the standard redox potentials:

$$E^\ominus(\text{H}_2\text{SO}_3/\text{HS}_2\text{O}_4^-, \text{H}^+) = -0.08 \text{ V}$$

$$E_{\text{B}}(\text{2SO}_3^{2-}/\text{S}_2\text{O}_4^{2-}, 4\text{OH}^-) = -1.12 \text{ V}$$



The reduction can be accompanied by chelation, for instance with the hexadentate ligand EDTA as its tetrasodium salt, which provides an alkaline environment that is optimum because the formation constant for the Fe(II)EDTA complex K_f has a peak value of 2×10^{14} at pH ~10. This method was first described by Helen Burgess,⁶⁸⁶ and has been investigated and developed as a conservation treatment for Platinotypes by Jacquelyn Rees and Megan Gent while researching at the V&A.⁶⁸⁷ Iron stains were removed very successfully from a number of historic Platinotypes by a process of reduction with sodium dithionite solution and chelation by tetrasodium EDTA. Deriving from this work, the author has found that an effective and convenient treatment is immersion for *ca.* one hour at room temperature in an aqueous solution 5% w/v in each of sodium dithionite and tetrasodium EDTA, at pH ~9. The same procedure needs to be tested on yellowed Palladiotype simulacra, to determine if it causes any image loss.

Matthew Clarke and Dana Hemmenway in their research at the NGA employed a protocol of immersing aged and stained test specimens in the chelate bath for 2–4 hours, then re-ageing the cleared result to see if stain re-appeared. They tested baths of 0.1 M Na_4EDTA , with and without added dithionite, and some of the newer and more powerful chelating agents such as DTPA, (diethylenetriaminepentaacetic acid) and HBED (bis(ortho-hydroxybenzyl)-ethylenediaminediacetic acid). The latter have larger K_f values, five orders of magnitude greater than EDTA. A solution of 0.01 M DTPA was found to be more

effective than EDTA in removing iron, especially when used in concert with 2% sodium dithionite at pH 8.⁶⁸⁸ HBED, however, gives a strong pinkish-red coloration with Fe(III) which can necessitate excessively long washing (ca. 22 hours) to accomplish its removal.

Ascorbic acid is also a convenient reducing agent, having a redox potential varying from -0.283 to -0.066 V as the pH varies from 2 to 7,⁶⁸⁹ which make it another possible reductant for Fe(III), but more effective in acidic conditions.⁶⁹⁰

Finally it may be observed that the iron-stain can be avoided entirely by printmakers today, even in palladium printing, by using – instead of hydrochloric acid – for the clearing baths, a reducing agent in concert with a modern chelating agent such as EDTA to clear the print as described in the Malde-Ware method, §7.22 (see also §10.9 and §10.10). Artificially accelerated ageing of Malde-Ware prints has been shown to produce no stain. Sodium disulphite reduction is also now routinely incorporated in the modern procedure for clearing other siderotypes recommended by the author (see §7.22).⁶⁹¹

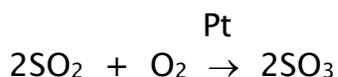
9.7 Acidity catalysed by platinum

The catalytic effect of 'platinum black' in Platinotypes has been blamed for their fragility. The issue of acidic embrittlement of the paper substrate of historic platinotypes is well-known to photograph conservators. The phenomenon is history-dependent: in the typical domestic atmospheres of the late Victorian era, when many historic platinotypes were made, gas, coal and coke were burnt openly in confined environments, as well as being present in the industrial discharges to the atmosphere.

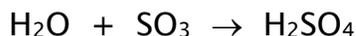
Sulphur dioxide from the polluted atmosphere is not itself the most serious threat, because with water it forms sulphurous acid, H_2SO_3 , which is relatively weak, and on drying it the SO_2 is lost again as a gas by the reverse reaction:



The embrittlement has been attributed to the platinum metal catalytically promoting the oxidation of the gaseous sulphur dioxide, SO_2 to sulphur trioxide, SO_3 :



with which water irreversibly forms sulphuric acid H_2SO_4 :



which is non-volatile and concentrates in the cellulose fibres, splitting the chains and weakening the structure. An unpublished experiment tested this general idea in 1989:⁶⁹²

- (1) A piece of cellulose paper was half-coated with platinotype sensitizer, exposed to UV light, and fully processed to produce an area of maximum density of black platinum.
- (2) It was cut into four pieces, two white, two black.
- (3) One white and one black piece were separately macerated in a liquidizer, and the pH of each measured instrumentally as a 'control'.

- (4) The other white and black pieces were exposed to an atmosphere of sulphur dioxide gas (ca. 1 atmosphere) for 3 days in a closed vessel.
- (5) These two were then 'pulped' and their pH's read, with the results:
- | | | |
|-------------------------|-----------------|--------------|
| Controls: | white paper 6.3 | black Pt 6.1 |
| SO ₂ Gassed: | white paper 4.5 | black Pt 2.6 |

These rough figures seem to provide preliminary evidence that 'platinum black' catalyses strong acid formation in the paper. The topic deserves full investigation with control of parameters such as relative humidity.

If one assumes a concentration/time reciprocity law for the "gassing" (I have no evidence that this is valid!) then 1 atmosphere of SO₂ for 3 days is about equivalent to a concentration of 100 ppm for 80 years. This is still an unreasonably high SO₂ gas exposure for an historic platinotype: outside levels could be about 1 ppm., indoors maybe more. Figures for the SO₂ content of the atmosphere at various times and places are available.⁶⁹³ For instance the Great London Smog of 1952 saw a rise to a maximum value of SO₂ level quoted as 1.34 ppm, compared with a previous mean of about 0.1– 0.2 ppm. Since the Clean Air Acts of the late 1960s, levels of SO₂ in some places in the UK (e.g. Manchester) have dropped by a factor of 10, from about 0.5 ppm to 0.05 ppm.

9.8 Offset imaging: "autoplatinography"

Platinum prints are sometimes observed to generate – spontaneously – a positive mirror-image in a light brown colour on the facing paper, card or tissue sheet with which they have been in contact for a long time.⁶⁹⁴ The writer has examples of such images offset from platinotypes bound into books, usually ca. 100 years old, but it is not known how long it takes to become perceptible – probably decades – because it has been observed most frequently in books and albums where the contact has been longstanding, see Fig. 9.4.

This kind of image transfer is reminiscent of Ostwald's "Catatype" process (§2.2); it has been little investigated up to 2012,⁶⁹⁵ but has recently aroused the interest of archive conservators in the USA, as described below. It is sometimes referred to colloquially as "ghosting" or "offsetting" but, since it does not yet appear to have been invested with a dignified name, I suggest the term *autoplatinography* for the phenomenon.⁷

It is unlikely to be due to the migration of substances out of the original image-bearing sheet – although such physical transference has occasionally also been observed in photogravures, where it can be attributed to constituents of the printers' ink not being fully dried. However, there is no evidence for the bodily transfer of solid or liquid image substance from a well-processed platinotype. It is more probable that autoplatinography is a chemical effect due

⁷ *Etymological footnote 7: the neologism "autoplatinography" is put forward here by analogy with the rather rare and obscure word "autobotanography" which has been used to describe the making of plant photograms in cyanotype by Anna Atkins. However, the origination of this word may be attributed to the novelist Jocelyn Brooke (1908–1966), who coined it in 1949 as a description of his 'botanical' autobiography The Military Orchid.*

to the high catalytic activity of 'platinum black' (*i.e.* nanoparticle platinum metal) promoting degradation reactions to form chromophoric groups within the contacted sheet. At least five contributing mechanisms, not mutually exclusive, seem possible here:

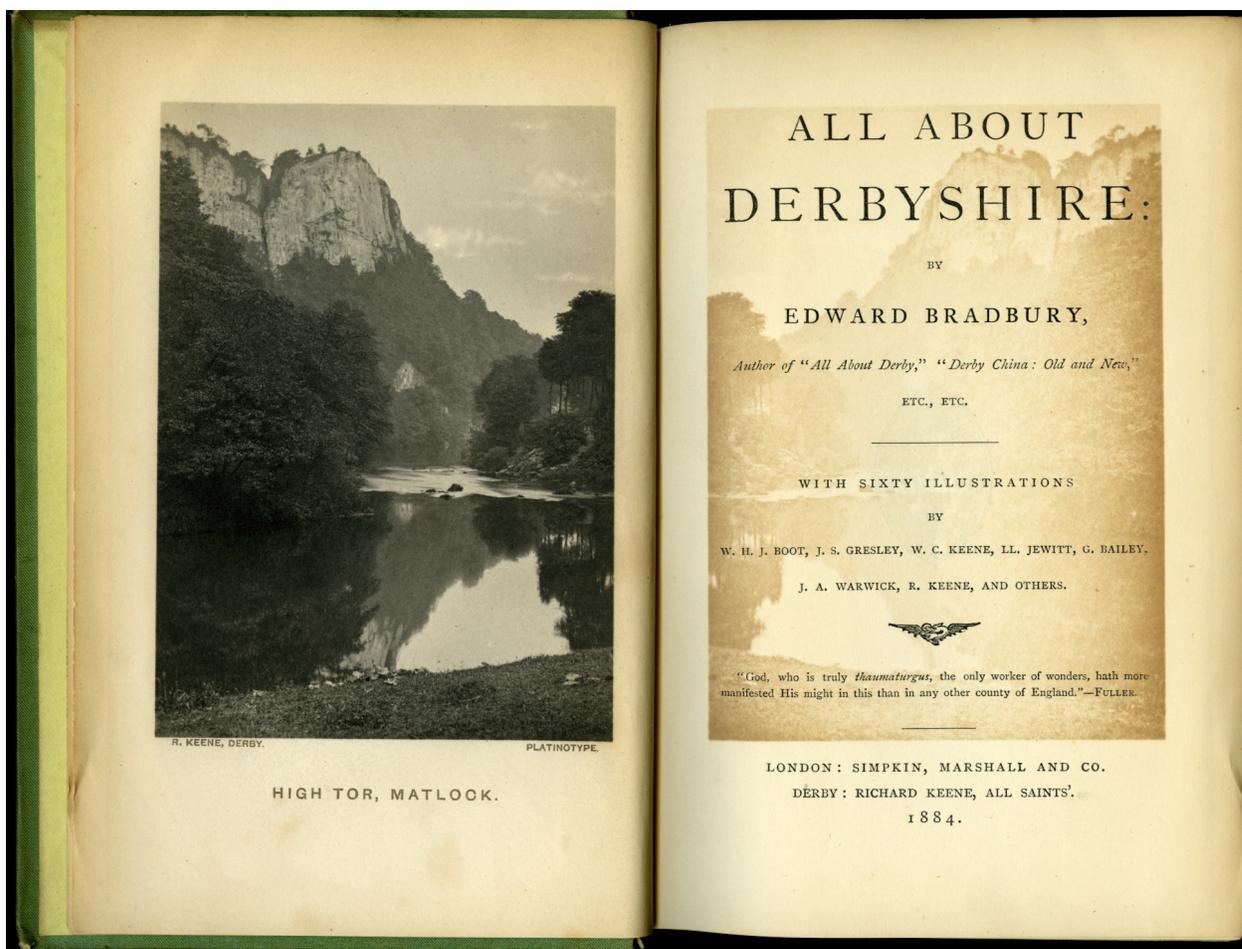


Fig. 9.4 Image offsetting by a bound-in platinotype: "Autoplatingraphy"

1) The catalytic production of acid (H^+) by the platinum black from atmospheric gases, as described in §9.7 above, and the highly mobile hydrogen ions degrading the opposite contacting sheet. However, acid alone does not necessarily cause strong colorizing of cellulose – for instance, the process of 'parchmentization' with strong sulphuric acid (§5.7) is not observed to stain the sheet. The sharpness of the images also suggests that diffusion is very restricted.

2) A direct catalysis by the platinum black of the oxidative degradation by the atmosphere of the lignin in papers that contain wood-pulp. Lignins are polyphenolic macromolecules, polymers of p-hydroxycinnamyl alcohol and its methoxy derivatives, which when oxidised give rise to conjugated quinoid structures having chromophores that impart a typical yellow-brown colour. Similar quinone chemistry causes the familiar yellowing of newsprint and the brownish colour of oxidised photographic developers containing hydroquinone.

3) Cellulose itself is less readily oxidised to coloured decomposition products than are lignins – but one cannot exclude this possibility in autoplating because it has been shown that oxycelluloses can give rise to condensed furan derivatives which impart a yellow colour to the substrate.⁶⁹⁶ Depending on the nature of the oxidant, other coloured oxidation products of cellulose may be generated; for instance, nitrogen dioxide – a possible decomposition product of images coated with collodion – can oxidise cellulose to yellow coloured diketones and brownish pyrones.⁶⁹⁷

4) If gelatin is present as a sizing agent in the contacted paper sheet it is conceivable that platinum black may catalyse a Maillard reaction between amines resulting from the degradation of the gelatin and any reducing polysaccharides (hemicelluloses in the keto form) present in the sheet, with the formation of typically brown-coloured condensation products. The reactive carbonyl group of the sugar reacts with the nucleophilic amino group of the amino acid, and forms a complex mixture of poorly characterized molecules responsible for yellow-brown colours and – in cooked foodstuffs – a range of aromas and flavors.

5) Any residual iron(III) in the platinum image may promote the formation of free radicals such as hydroxyl and hydroperoxyl (§10.4), which then through diffusion could create coloured decomposition products in cellulose sheets.⁶⁹⁸

All five of these possibilities are entirely hypothetical at present, and call for further investigation; they depend on the composition of the contacted sheet, so could be tested by careful analysis of the contacted papers in real specimens, for lignins, gelatin, etc, and examination of the image areas by UV-visible, infrared, and Raman spectroscopy, to detect and confirm the chromophoric organic functional groups.

Autoplating in books frequently show the strongest densities at the borders of the page, fading towards the centre, see fig. 9.4, suggesting that ingress and diffusion of the atmosphere around the edges of the page may have played an essential role in promoting the degradation reaction in these cases. It is not known whether the oxygen of the atmosphere alone can cause autoplating, or whether pollutants such as sulphur dioxide or nitrogen dioxide are also necessary.

Recently, investigation of the “ghosting” phenomenon in 2013–4 by a team of researchers at the National Archives and Records Administration, (NARA) in Washington DC, has clarified some of the circumstances of its occurrence, and apparently eliminated some of the speculations listed above.⁶⁹⁹ The NARA team studied a number of examples of autoplating formed on a range of substrate papers by historic platinum-toned matte collodion prints and by pure platinum prints. Rebinding of albums was observed to have produced different superimposed images, with a history that suggests the phenomenon can arise within less than 50 years. A wide range of modern instrumental methods and spectroscopic techniques was brought to bear on selected examples in an attempt to characterise the nature of the image substance.⁷⁰⁰ In all cases no differences could be detected by any of these techniques between the light and dark areas of the ghost image and the blank paper surrounding it. One must conclude that the image substances were effectively so 'dilute' in the chosen

specimens that their characteristic spectra did not show above the instrumental noise levels. The autoplatingrams were also found to be substantially lightfast to the level of Blue Wool 3, and there was absolutely no evidence for the transfer of image metal.

These researchers were, however, able to generate their own "ghost" images by accelerated ageing of historic platinum-toned matte collodion photographs, which had a history of causing ghosting, contacted under pressure with six different substrate sheets (five of them 100% cellulose of various pH, weights and surfaces, one a newsprint containing lignin), typically at 85 C and 65% RH for 4 weeks. Four of the five cellulose papers showed ghost images, some faint, but the lignin-containing paper did not, thus clearly demonstrating that the presence of lignin is not essential to the phenomenon.

Because of the possibility that the collodion print could cause ghosting by the nitrogen dioxide degradation product of the collodion (a nitrocellulose) present, a true platinum print was also similarly tested on two 100% cellulose papers, and found to form ghosts on both. Penetration of the ghosting through an interleaving sheet was also simulated, suggesting a gas phase transferral. The ghosting phenomenon seemed to be independent of the presence of any alkaline buffer, and the ghost image could not be washed out with water. In contrast, specimens of platinum prints with no history of autoplatingraphy gave negative results with the accelerated ageing contact tests, showing that the phenomenon is selective – for reasons not yet understood. Examination of the laboratory-produced ghosts by the whole range of spectroscopic techniques used earlier, produced equally negative results to distinguish the substance of the ghost image from its clear substrate. The chemistry of this phenomenon of autoplatingraphy remains to be elucidated, and will require stronger "ghost" images and more sensitive spectroscopic techniques, persistently applied.

It is however clear from these specimens that contact is not essential for the process, which may therefore involve gaseous species (singlet state molecular oxygen?), because the effect can be seen to penetrate a facing guard tissue and be imprinted on the opposite page, (Fig. 9.5) and it can even penetrate through the verso of the sheet bearing the platinum print, to be transmitted faintly to the previous page.⁷⁰¹

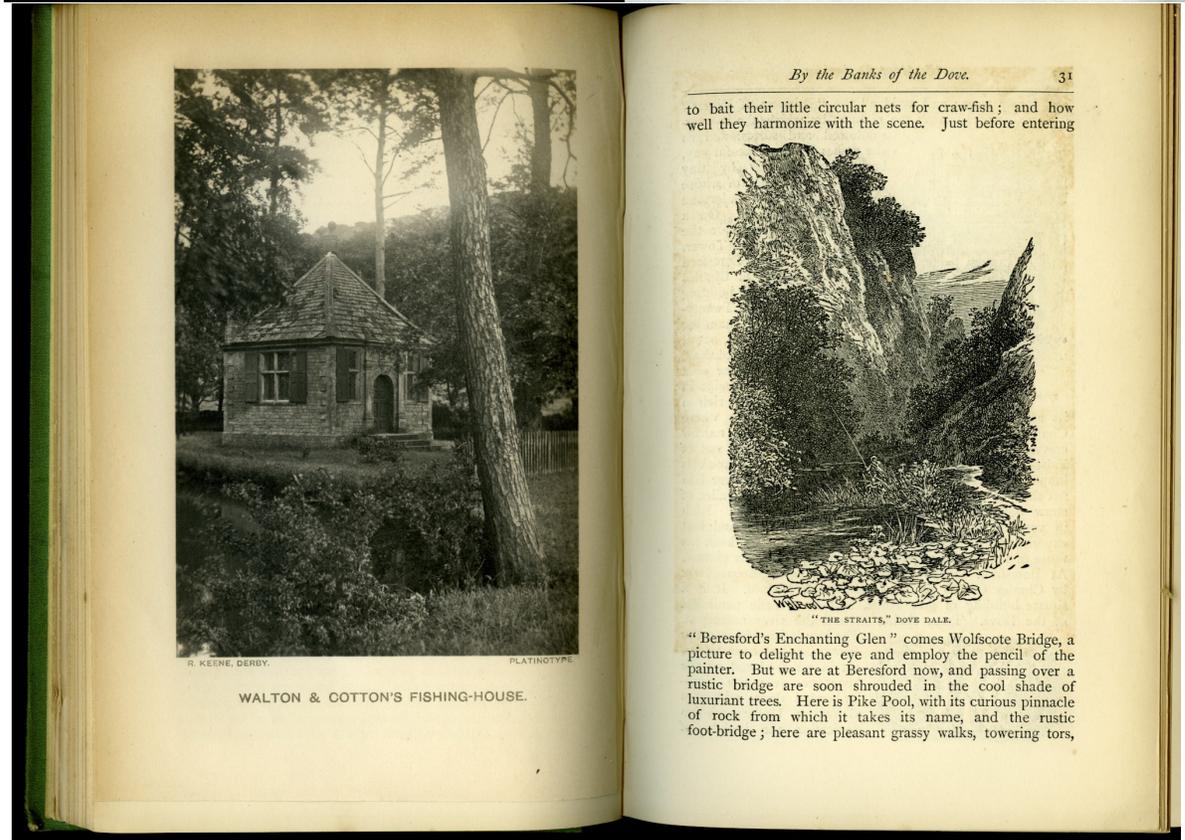
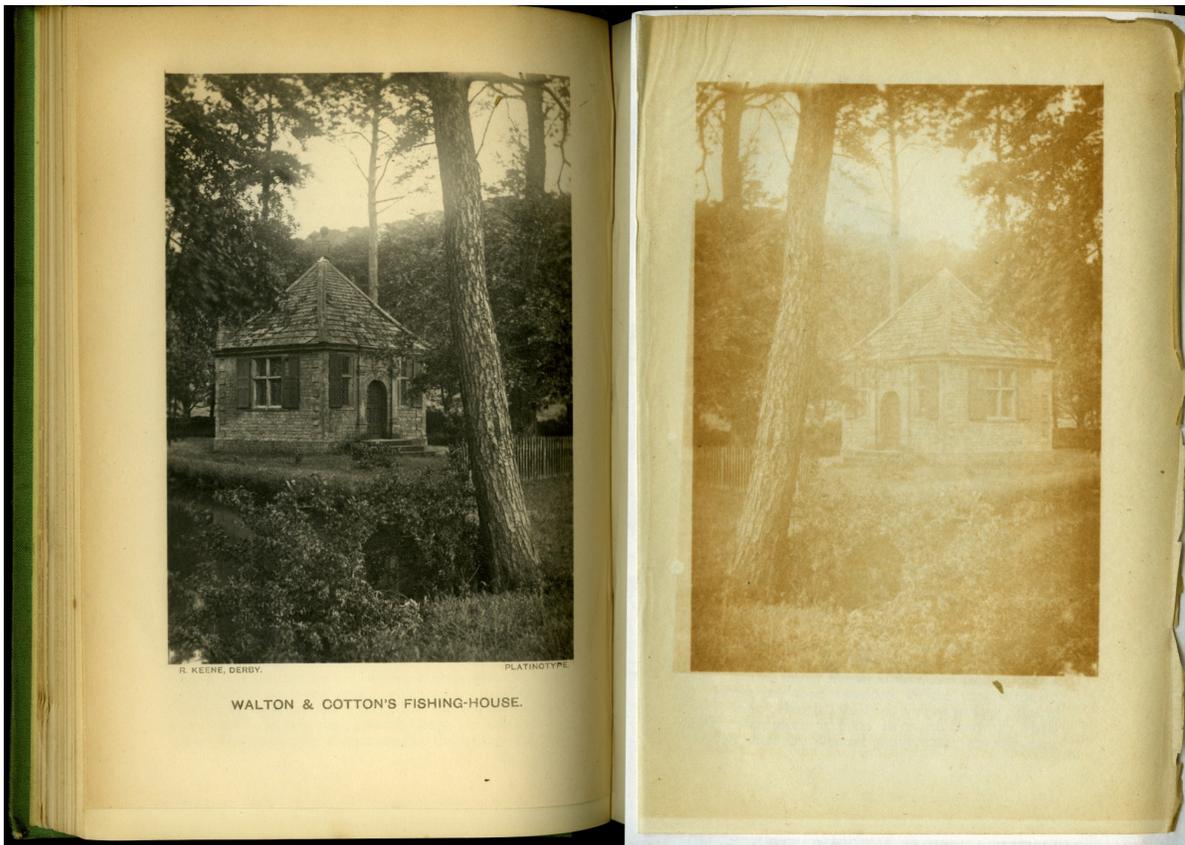


Fig. 9.5 Penetration of platinum offsetting

So far, I have only seen one case of this phenomenon being caused by palladium prints⁷⁰² – but that may only be due to their relative scarcity or more recent provenance. From the specimens used by the NARA researchers, it appears that the phenomenon can also occur with "faux platinum" silver papers that have been platinum-toned, such as "Aristo-Platino" paper (Fig. 9.6).

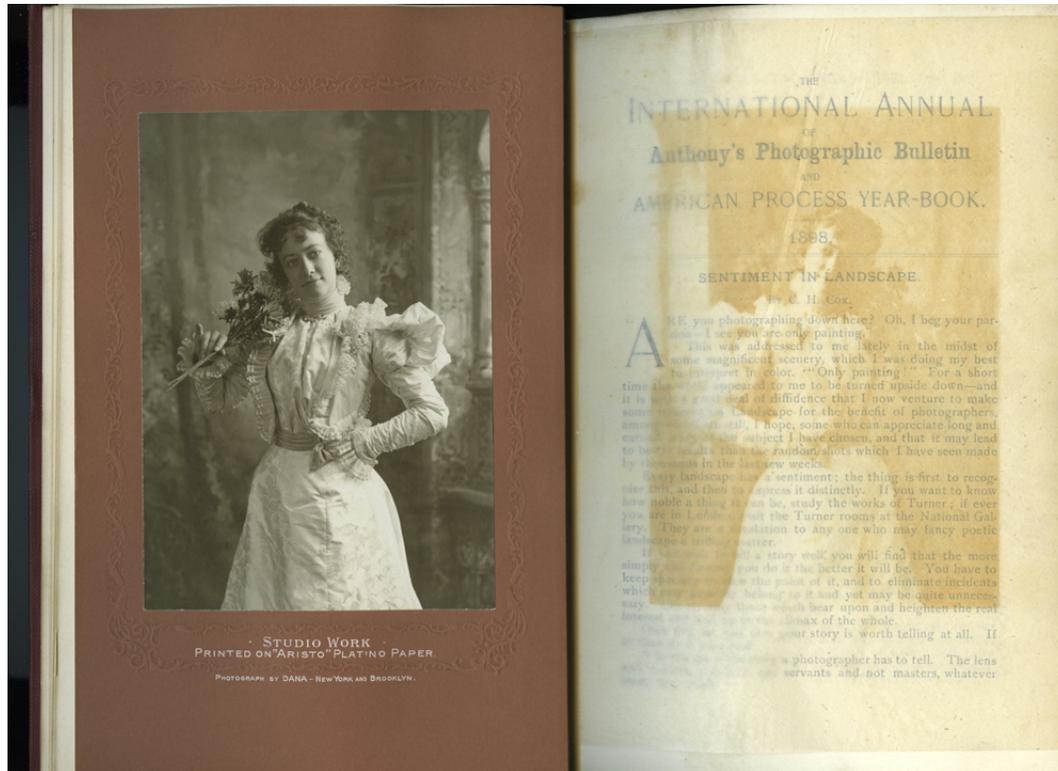


Fig. 9.6 Image offsetting by a platinum-toned 'Aristo' Platino print

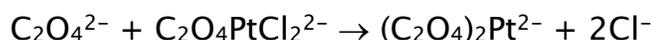
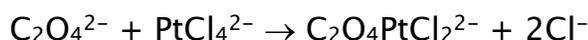
There are some rare instances of untoned silver prints on specialist papers also causing such offsetting in facing papers of high cellulose content, so the platinum-catalysed degradation cannot be the sole explanation.⁷⁰³ Further research into autoplating and related phenomena, by ultraviolet, infrared and Raman spectroscopy etc., would seem desirable.

9.9 Age deterioration of Platinotype paper

It was commonly held, both by practitioners and suppliers of platinum papers, that "water is the great enemy of the Platinotype". But this cannot be strictly true: aqueous solutions are used both to coat and to process Platinotype papers, so water is not the enemy *per se*. Rather, water provides the battleground for the potential combatants, enabling their solubilization, and thereby accelerating the slow decomposition reactions under humid conditions.

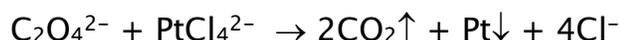
Many of the additives used in modern papermaking are potentially hostile to the iron or platinum chemistry, especially alkaline buffers such as chalk, which causes hydrolysis of the iron(III); but chalk was not added to C19th papers, which were acid-sized with alum-rosin. Gelatin size tends to bind to the platinum(II) and render it non-reducible, lowering the sensitivity, so Willis avoided it in his papers.

There is the possibility of the iron(III) binding to cellulose, a process that would generate free oxalate ions. If any significant concentration of free oxalate is built up, it may displace chloride ligands and form more stable chelated oxalatoplatinum(II) complexes:⁷⁰⁴



The resulting oxalatoplatinate(II) complexes will probably be more resistant to reduction by iron(II) to form the image, again lowering the sensitivity.

There is also the further possibility that oxalate anion itself can reduce platinum(II) to the metal:



a reaction that is thermodynamically allowed by the redox potentials:

$$E(\text{PtCl}_4^{2-}/\text{Pt}, 4\text{Cl}^-) = +0.73 \text{ V}$$

$$E(2\text{CO}_2, 2\text{H}^+/\text{H}_2\text{C}_2\text{O}_4) = -0.49 \text{ V}$$

and would cause a grey/black fogging of the paper in the dark, especially if humid, before any exposure or processing; albeit this reaction is probably very slow with platinum, it has been observed with palladium. The two foregoing reactions also account for the failure of Willis's short-lived "platinum-in-the-bath" process of 1888–1892, described in §1.7, owing to the decomposition of the developer solution, which contained a mixture of concentrated potassium oxalate and potassium tetrachloroplatinate(II), with the formation both of oxalatoplatinates and the precipitation of platinum metal.

The third, and most probable route for deterioration of long-stored, dry platinotype paper is simply the very slow thermal decomposition of the ferric oxalate in the dark by an internal redox reaction, the same as the photochemical reaction, to yield some ferrous oxalate:



This would not be apparent in the stored dry paper, which would remain pale yellow, but would immediately become evident upon wet processing with oxalate which solubilises the Fe(II) to reduce the Pt(II) and cause a grey fog of Pt metal to appear in the highlights. The spontaneous decomposition of ferric oxalate is reflected by its apparent absence in nature: while ferrous oxalate dihydrate, $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ occurs naturally as the mineral Humboldtine (or Humboldtite),⁷⁰⁵ naturally-occurring ferric oxalate has never been found or reported – despite the abundance of ferric oxides as iron minerals. From the point of view of redox chemistry, ferric oxalate is a self-destructive substance!

Given this background chemistry, we can now understand why Willis's commercial papers were marketed in solder-sealed tins (Fig. 1.14, §1.14), containing a desiccant of anhydrous calcium chloride, usually dispersed onto asbestos wool to provide a large surface area and facilitate occasional regeneration of the desiccant by strong heat. With very little water present, the degradation reactions are greatly slowed up. Sealed tins of Willis's papers

opened in modern times after *ca.* 100 years show varying degrees of deterioration, depending on the grade: a specimen of Japine paper opened in 2013 was very dark overall; whereas KK and AA papers appeared only buff and still retained slight light-sensitivity.⁷⁰⁶ The photohistorian, Rob McElroy, has acquired a number of specimens of unused platinotype papers for his collection,⁷⁰⁷ and has opened some of the sealed tins to provide samples for analysis. Photograph conservator Margaret Wessling has found that one of these specimens, approximately 100 years old, of a pale yellow colour, still retains considerable photosensitivity for printing images, although the high values come out uniformly fogged to a mid-grey, as predicted above.⁷⁰⁸

When platinum paper is hand-coated and used the same day, the need for desiccation disappears, so self-coated papers can be used at higher RH than was the commercial product, with some benefit to the image quality. However, according to some contemporary practitioners, even storing the coated paper overnight, at normal temperature and humidity, can lead to a perceptible flattening of the contrast.

9.10 Diagnosis of fogged images

A common fault observed in many handmade prints is highlight fogging – the appearance of tone due to image substance (platinum and/or palladium) being deposited where there should be none. It should be appreciated that the chemical thermodynamics as summarised in §11.3 predict that free oxalic acid is capable of completely reducing tetrachloroplatinate(II) or tetrachloropalladate(II) to the metal. However the rates of these reactions are generally slow, compared with the time of processing a print, unless accelerated by a higher temperature or possibly self-catalysis. Nonetheless, if free oxalic acid is present in the sensitizer, the reactions may proceed sufficiently to cause a perceptible fog. There are at least six possible causes of this fault, so there now follows a systematic method of diagnosis. Note that it is important for reference and comparison, to have a margin of clear paper which has not been coated with sensitizer, and a border which has been coated but remained masked and unexposed, as described in §7.16.

9.11 Black spots in platinum–palladium prints

Related to fogging is the notorious "plague of black spots" that sometimes afflicts contemporary platinum–palladium prints made by the iron(III) oxalate development process.⁷⁰⁹ The nature and cause of this destructive and frustrating phenomenon are both uncertain. It is supposed that the black spots consist of the noble metal, but this has not yet been proved by EM/EDX. Such flaws have been attributed, especially in the early literature,⁷¹⁰ to the presence of small particles of iron or other metal in the paper sheet, and variously blamed on the cotton–picking equipment, the Hollander beaters used for pulping, the papermaking machine, or even burring of the guillotine blade used for cutting the sheet; but these speculations are not supported by all the observations. Such metal particles, if present, should be visible in the untreated sheet under a lens or microscope, and can usually be removed by the tip of a scalpel. Moreover, metallic iron being a strong reducing agent, these particles should react immediately with the sensitizer solution on coating, to produce tell–tale deposits of platinum or palladium metal, appearing as black streaks which follow the direction of the coating, showing characteristic 'meteor tail' shaped patterns.

Spots which are not of this kind are clearly particulate, of a diffuse circular shape, and randomly distributed within the coated area, but may also form outside the exposed picture area. Their occurrence is found to be paper–dependent; characteristically – and most frustratingly – they are only seen *after* development, and they appear to increase in number and density with the vigour of the developer (*i.e.* oxalate produces a worse effect than citrate). Their appearance also seems to be more common with palladium than with platinum, possibly due to the higher reactivity of the former.

One hypothesis is that they may be due to microcrystals of iron(II) oxalate having been precipitated in the coated layer by reduction of the iron(III) oxalate sensitizer by impurities in, or additives to, the paper: substances which also happen to be reducing agents, such as aldehydes (used to harden gelatin size) or sulphites (used in pulp treatment). Iron(II) oxalate forms insoluble yellow particles (microcrystals) which would be invisible in the yellow sensitized layer, and their presence would only become apparent when solubilised by the developer to react with the noble metal salt. It may be significant that the black spots have never been observed with the print–out Malde–Ware platinum–palladium version (§7 and §11.2) using ammonium iron(III) oxalate which, if accidentally reduced, would produce a soluble iron(II) product which would disperse, instead of particles of insoluble ferrous oxalate.

As for treatment: spots of palladium may be etched out with dilute hydrobromic acid, plus an oxidising agent such as ferric bromide or potassium bromate, as described in §7.23. Any solution containing bromide ion, an oxidising agent, and acidified with a dilute mineral acid should be effective.

According to Ian Leake, filtration of the sensitizer immediately before coating does not ameliorate the problem, suggesting that, in his instance of the affliction at least, the particles are not present in the iron(III) oxalate stock solution itself. However, he finds filtration of the developer to be beneficial – an observation which suggests that the origin may be particles from the developer

– which differs from the hypothesis above.⁷¹¹ It should be remembered that any re-used platinotype developer will always contain excess sensitizer reagents in solution, and will therefore still be photosensitive; if it is not totally protected from actinic light, it will steadily precipitate particulate platinum metal, which if left in suspension could find its way onto the surface of subsequent prints.

9.12 Fading of Platinotypes and kelainotypes

Pure platinotypes cannot fade, because there is no substance commonly present in a normal 'studio' environment that can oxidise, dissolve or react with metallic platinum in any way. *Aqua regia* is the only well-known solvent for platinum but is hardly likely to be present in a studio, museum or gallery. Nonetheless, deterioration by image loss has been observed in some instances of historic "platinotypes" in collections. Any fading of a supposed "platinum print" must therefore be due to the loss or transformation of *some other substance* in the image – probably a metal. Silver and mercury are the most likely candidates, which are present in "Satista" and "Sepia" platinotypes, respectively. It has been noted that some of the Platinotypes that have suffered significant fading are those by Eva Watson-Schütze and Sarah Sears, ca. 1900, in the Library of Congress Collection.⁷¹² All these faded prints are believed from their XRF spectra to have been mercury-developed, see §5.9 and §6.7, and if the quantity of mercury used was excessive, or the precipitation of platinum was inhibited for some reason, this loss of image density must presumably be due to the volatility of the mercury metal in the image allowing evaporation, because mercury does not form an amalgam with platinum, which would otherwise lower its vapour pressure and greatly slow evaporation – see §11.9.

In this connection, it is significant that all the known specimens of the 100% mercury prints made by Herschel in the 1840s have always faded completely.⁷¹³ Of all Herschel's siderotype investigations, the most tantalizing proved to be this *kelainotype* process, as he called it.⁸ This process apparently furnished images in metallic mercury which could display visual qualities so rich and unique that Herschel was completely seduced:

"[Kelainotype]... affords pictures of such force and depth of colour, such velvety richness of material, and such perfection of detail and preservation of the relative intensities of the light, as infinitely to surpass any photographic production I have yet seen, and which indeed it seems impossible to go beyond."⁷¹⁴

But there is a problem with this sumptuous process: as stated above, mercury is volatile at room temperature and evaporates.⁷¹⁵ To his chagrin, all of Herschel's kelainotypes faded within a few days, provoking his frustrated comment:

"Most unfortunately, they cannot be preserved."

⁸ *Etymological footnote 8: probably taking the name from the Greek word for 'dark', kelainos = κελαινος, but sometimes transcribed as celænotype – possibly a reference by Herschel to Celæno – a member of the mythological band of malevolent Harpies who specialised in torturing men.*

Fully authenticated specimens of kelinotype, with Herschel's handwritten annotations on the *verso*, exist in the collections of the National Media Museum, Bradford UK and the Harry Ransom Center, Austin, Texas. They are all now no more than yellowed rectangles of paper bearing no discernable images. Herschel expended much time and effort in endeavouring to improve the procedure for the mercury print, but ultimately without success. His exasperation as a scientist is evident in a letter to Talbot:

"It has led me such a dance as I never before was led by any physical enquiry..."⁷¹⁶

The problems that Herschel encountered with his evanescent kelinotypes remain unsolved to this day, but the lesson for contemporary platinum printers is clear: do not over-use mercury(II) additives.

9.13 Methods for toning Platinotypes

There are many photographic printers – including this author – who believe that to tone a platinum or palladium print is an act of philistinism, comparable with those superfluous gestures memorably ridiculed by William Shakespeare:

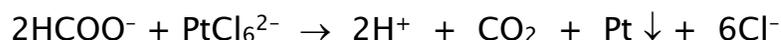
"To gild refinéd gold, to paint the lily,
To throw a perfume on the violet,
To smooth the ice, or add another hue
Unto the rainbow, or with taper light
To seek the beauteous eye of heaven to garnish,
Is wasteful and ridiculous excess."⁷¹⁷

Nonetheless, given that perversity so characteristic of early photographic experimenters, several toning methods were devised for platinum prints historically, so they must therefore be summarised here – albeit reluctantly and briefly. Unlike Packham's toning method, §9.3, which depended on an impurity of iron(III), all of them rely on the catalytic power of the platinum black to promote reactions which precipitate some foreign substance proportionally onto the platinum image; the underlying metal is itself unchanged, so the best that can be said of these procedures is that some do have the sole virtue that they may be removed again without much damage to the original print. Some of these toning procedures have a commonality with the composite printing methods, such as cyanotype over platinotype or palladiotype, described in §3.11. For more information on these methods and their relevance to the prevailing practices and aesthetic, the reader is referred to the article by Erin Murphy.⁷¹⁸

Silver may be deposited onto a platinotype by silver nitrate solution mixed with a reducing agent such as gallic acid, hydroquinone or pyrogallol – *i.e.* traditional silver developers. It imparts a reddish colour;⁷¹⁹ the silver may then be converted into platinum by chloroplatinite solution – "bringing coals to Newcastle", indeed!

Platinum may be used to intensify Platinotypes directly using a solution of 'platinic chloride' i.e. dihydrogen hexachloroplatinate(IV), and the reductant sodium formate, which catalytically deposits more platinum on the image:⁷²⁰

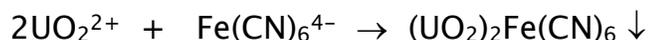
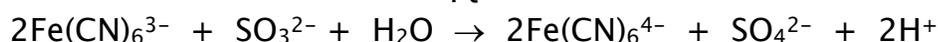
Pt



Uranium toning of platinotypes was probably introduced by Fitz-Payne in 1892,⁷²¹ and was taken up the following year by no less than Alfred Stieglitz,⁷²² but later it came to be associated with its prime exponent James H. McCorkle.⁷²³

The process employs an acidified mixture of uranyl nitrate and potassium ferricyanide, usually with sodium sulphite as the reductant which, catalysed by the platinum black, can reduce ferricyanide to ferrocyanide to precipitate the insoluble red pigment, uranyl ferrocyanide, onto the platinum image:

Pt



By using this toner on an uncleaned platinum print which still contains iron(III), Prussian blue (ferric ferrocyanide) can be formed simultaneously with the uranyl ferrocyanide, and mixtures of the two pigments – one blue, one red – will therefore produce a whole gamut of unattractive false colours in the image. As remarked by the editor of *Cassell's Cyclopædia*, this toning process :

"...does not give very permanent results" ⁷²⁴

Gold toning of platinotypes due to A.W. Dollond places a coating of glycerol over the print, then the application by brush of a solution of gold(III) chloride which, catalysed by the platinum, oxidises the glycerol to dihydroxyacetone or glyceraldehyde, being itself reduced to nanoparticle gold:⁷²⁵

Pt



The nanoparticle gold imparts a bluish colour to the image, and was used to intensify weak platinum prints. The treatment with gold was thought not to adversely affect print permanence; as one writer put it:

"In intensifying platinum prints with gold or with platinum there is at least the consolation for the trouble expended that the permanency of the image has not been tampered with." ⁷²⁶

Paul Strand's reported use of Dollond's gold toning for platinotype has been investigated by conservator Alisha Chipman, who has successfully replicated this toning procedure.⁷²⁷

10. Relevant Aqueous Chemistry of Iron(III)

The sensitizer solutions for platinotype and palladiotype contain dissolved iron salts that may not be fully removed from the print paperbase by the wet processing sequence, as described in the previous chapter, where some curative treatments for yellowed historic Platinotypes and Palladiotypes have already been examined. This chapter considers the aqueous chemistry of iron in more detail in order to arrive at preventative methods in the modern processing of such prints.

10.1 Summary for non-chemists

Iron(III) (aka "ferric" iron, Fe^{3+}) in contact with water, if not highly acidic, will slowly undergo (over days - weeks - years) a complicated sequence of chemical changes, dependent on the acidity or alkalinity of the solution, *i.e.* its pH. Undesirable changes can become effectively irreversible after the first day or two. The molecular structure of the "iron oxide-hydroxide" that is formed - effectively the same as "rust" - becomes progressively more extended or polymeric, and correspondingly more insoluble, and its colour shifts from near colourless through yellow to orange and even red, which is probably responsible for the disfiguring stains observed on some platinotypes and, especially, palladiotypes. Besides discoloring the image, the presence of iron(III) may also promote reactions that break the cellulose chains and weaken the paper structure.

There are at least three possible chemical stages in the mechanism for iron retention; but which of these apply in actual prints has not yet been elucidated, and should be an early experimental objective in contemporary research:

(a) the iron salts may be loosely adsorbed on the cellulose by relatively weak hydrogen bonds - these should be easy to wash out, avoiding hydrolysis;

(b) the iron(III) may be chemically bound at the molecular level (chemisorbed) as discrete iron(III) species to reactive groups (hydroxyl) on the cellulose that makes up fine paper. To remove this bound iron(III) will require powerful clearing agents;

(c) if nanoparticles of solid "iron oxide-hydroxide" are formed, they may be physically trapped within the microfibrils of the cellulose, and be very hard to dissolve or dislodge and remove.

Initially, alternatives (a) and (b) seem more probable, but lengthy exposure of an iron-stained object to a humid atmosphere could eventually lead to (c).

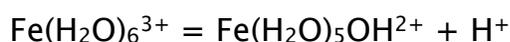
Successful removal of the iron(III) from platinum and palladium paper prints can be achieved by *reductive dissolution and complexation* in which the iron(III) is first reduced to iron(II), then bound in a soluble form and dissolved. Safe methods have recently been established and tested on historic Platinotypes by conservation scientists. The effectiveness of this method needs to be tested further for Palladiotypes, to ensure that it causes no harm to the image. It may then be considered a viable option for treatment of collection items.

Yellow stains could also be the consequence of residual platinum or palladium salts, or of the sulphiding of additives of lead, mercury or silver, or

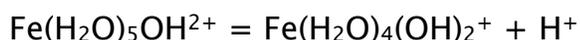
they could be due to the oxidation products of cellulose paper itself.⁷²⁸ These possibilities, if present, would require different treatments for their removal.

10.2 Hydrolytic reactions and colour

The hydrolysis of iron(III) has been studied for over 50 years, and evidence has been obtained for the existence of various polynuclear species.⁷²⁹ The following equations, with colours indicated by the wavelength of the absorption maximum, λ_{\max} , summarise the aqueous equilibria for simple Fe(III) dimers, the initial products that have been established and studied by several authors.⁷³⁰



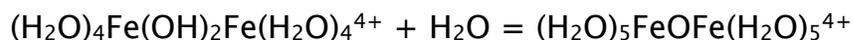
very pale $\lambda_{\max}=240$ nm yellow $\lambda_{\max}=297$ nm



yellow $\lambda_{\max}=300$ nm



greenish-yellow (μ_2 -dihydroxodiiron(III) cation) $\lambda_{\max}=335$ nm



deep orange-brown (μ_2 -monooxodiiron(III) cation)

The colours of simple iron(III) species in very dilute aqueous solution are determined by the wavelength maximum, λ_{\max} , of the nearest absorption band in the UV, which is due to an intense 'Ligand-to-Metal-Charge-Transfer' transition (LMCT for short), the 'tail' of which may encroach on the visible spectrum, absorbing blue light and therefore giving an appearance to the eye of the complementary colour – yellow. λ_{\max} moves to slightly longer wavelengths with lower energy of the LMCT transition, *i.e.* the increasing electron-donor ability of the ligand in the series: OH_3^+ , OH_2 , OH^- , O^{2-} , and the consequent absorption of green as well as blue light from the visible spectrum shifts the apparent colour slightly. However in non-dilute systems (condensed phases such as iron oxide polymers or solids, there is an additional effect: the interaction between adjacent iron centres via O bridges, for instance in dimeric μ_2 -monooxodiiron(III) units, $[\text{Fe}-\text{O}-\text{Fe}]^{4+}$, which gives rise to intense absorption bands in the spectra. As Sherman and White put it:

“Taken together, these results show that the ligand-to metal charge transfer transitions in Fe^{3+} oxides and silicates occur at energies much higher than those suggested by some previous investigators. The visible region absorption edge, which gives the iron oxides their red to yellow colors, does not result from ligand-to-metal charge-transfer transitions but is a consequence of very intense Fe^{3+} ligand field and $\text{Fe}^{3+}-\text{Fe}^{3+}$ pair transitions. Both types of transitions are Laporte and spin-allowed via the magnetic coupling of adjacent Fe^{3+} cations.”⁷³¹

The μ_2 -monooxodiiron(III) cation $[\text{Fe}-\text{O}-\text{Fe}]^{4+}$ has recently been proved to be the dominant dimeric species in aqueous solutions of iron(III) and has been characterised using EXAFS spectroscopy.⁷³² It is a much more highly-coloured

species than the monomeric $[\text{FeO}_6]$ chromophore, due to 'Metal-to-Metal Charge Transfer transitions (MMCT) mediated by the π orbitals of the oxo bridge and the antiferromagnetic superexchange between the coupled metal centres, as mentioned above.

It is now conjectured by the author that the μ_2 -monooxodiiron(III) cation $[\text{Fe}-\text{O}-\text{Fe}]^{4+}$, formed by the association of two adjacent Fe^{3+} centres bound to cellulose, may be the chromophore responsible for the notorious yellow stains that can slowly develop in platinotypes and palladiotypes on a cellulose substrate contaminated with residual Fe(III) as described in §9.2.

Further oligomerization is possible with bridging bidentate ligands having a small 'bite', such as sulphate or acetate (ethanoate), which promote formation of the stable triangular core $[\text{Fe}_3\text{O}]^{7+}$ which has more delocalized orbitals for the MMCT electronic transition at lower energy and is consequently very deeply coloured, e.g. basic ferric acetate:



deep red (hexakis- μ_2 -acetato- μ_3 -monooxotriiron(III) cation)

For this reason, acetic acid is not a good clearing agent for siderotype processes, and citric acid is preferable.

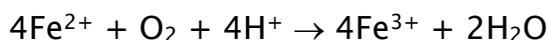
10.3 Hydrolysis and precipitation

The hydrolysis of iron(III) at room temperature proceeds in four stages:⁷³³

- 1) Hydrolysis to mono- and dimers, rapidly-established equilibria are reversible by lowering the pH, as described in §10.2 above,
- 2) Reversible rapid growth (on a timescale of minutes) to oligomers and small polymers: a non-precipitated sol is formed, called "red cationic polymer", consisting of linked octahedra of $[\text{Fe}^{3+}(\text{O}^{2-}, \text{OH}^-, \text{OH}_2)_6]$ approximating to $\text{Fe}(\text{OH})_{2.5}^{0.5+}$ of 2–4 nm sized nanoparticles, each containing ~100 Fe atoms.
- 3) Formation (on a timescale of days to weeks) of slowly reacting larger polymers, of 20–50 nm size, which agglomerate anisotropically and irreversibly into linear chains –rods– and sheets –rafts.
- 4) Eventual precipitation (on a timescale of years) of a solid phase: crystallization leads to the formation of highly insoluble 3-D lattices of deep red-brown Goethite, $\alpha\text{-FeO}(\text{OH})$, and Haematite, $\alpha\text{-Fe}_2\text{O}_3$.⁷³⁴

10.4 Free radicals

Fe(III) trapped in paper can suffer photochemical reduction to Fe(II), and in the process cause degradation of the organic molecules.⁷³⁵ Molecular oxygen from the air can re-oxidise Fe(II) (slowly in acidic and rapidly in basic solution):



but the mechanism of this re-oxidation also involves intermediate free radicals.

If peroxides are present, the Fenton reaction can produce free radicals:⁷³⁶



This is truly catalytic because of the further reaction regenerating Fe(II):



The $\bullet\text{OOH}$ and $\bullet\text{OH}$ free radicals so produced are very reactive and can oxidise organic compounds, causing scission of the cellulose chains: depolymerization, and damage due to loss of fibre strength.

10.5 Coordination by oxalate

Polycarboxylates of iron(III), *i.e.* oxalate or citrate complexes, are central to the functioning of the photosensitizers in all the siderotype processes, but some aspects of this chemistry remain yet to be fully elucidated. If the molar ratio of iron:oxalate is 1:3 or greater, then the predominant species will be the simple, monomeric trisoxalatoferrate(III) anion, $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$, a tris-bidentate octahedral complex, symmetry point group D_3 – a chiral molecule shaped like a ship's propellor:

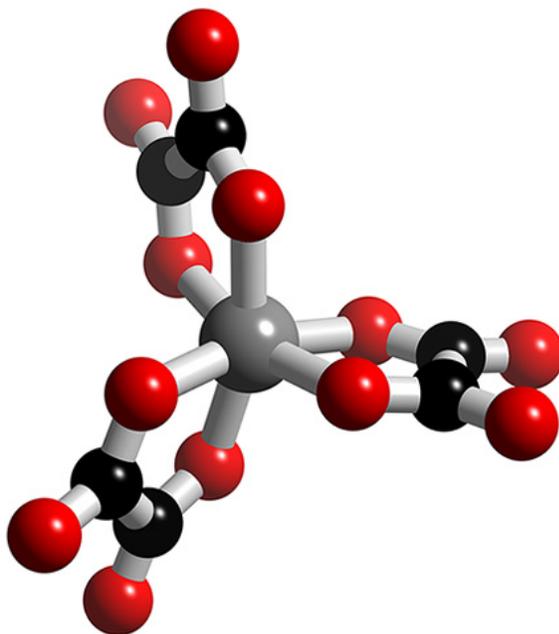
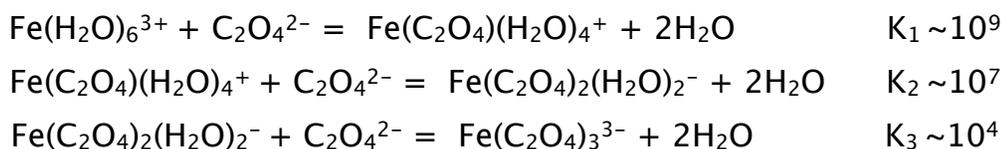


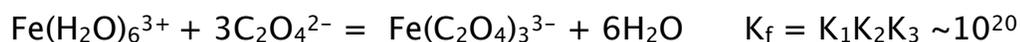
Fig. 10.1 Structure of the trisoxalatoferrate(III) anion $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$

It is present in the salt, ammonium iron(III) oxalate, more correctly known as ammonium trisoxalatoferrate(III), which is preferred for the photochemistry in the Malde–Ware updated Pt/Pd process, because this well-characterised pure complex salt dissolves easily, is stable indefinitely, and provides a predominantly 'print-out' process, as described in §7.⁷³⁷

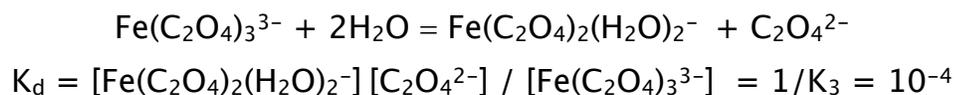
The stepwise formation constants for $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ are approximately:⁷³⁸



The overall formation constant, K_f for the tris-complex is the product of these:



The value of the third step-wise formation constant K_3 implies that, in a concentrated (~ 1 molar) solution of the trisoxalatoferrate(III) anion, there is sufficient dissociation of the complex to form about 0.01 molar free oxalate anion in equilibrium:



$$\text{Now } [\text{Fe}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-] \approx [\text{C}_2\text{O}_4^{2-}] \text{ and } [\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}] \approx 1$$

$$\text{so } [\text{C}_2\text{O}_4^{2-}] \approx \sqrt{(1/K_3)} = 10^{-2}$$

It should be borne in mind that oxalate anion can react with some metal cations such as silver and gold, so this small presence of free oxalate can give rise to reactions (§11.12). It may also cause a small amount of the sparingly soluble salt, ammonium oxalate, to crystallise out as colourless needles from concentrated solutions of ammonium iron(III) oxalate in water (§7.6).⁷³⁹

The complexation of Fe(III) by oxalate has a marked effect on the redox potential, which is diminished from the standard value typical of Fe(III) as a moderate oxidising agent:

$$E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.771 \text{ V}$$

to a value for the chelate of:

$$E(\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3^{3-}/\text{Fe}^{\text{II}}(\text{C}_2\text{O}_4)_2^{2-}) = +0.02 \text{ V}$$

indicating that the Fe(II) complex has become a moderate reducing agent. This difference in E is a consequence of the much stronger coordination of oxalate to Fe(III) with $K_f \sim 10^{20}$ than to Fe(II) with $K_f \sim 10^5$. The other aquated species indicated in the equilibria above will have redox potentials intermediate between these extreme values.

The equilibria represented above by K_d are displaced if excess oxalate anion (as ammonium oxalate) is added to the sensitizer solution: by the Law of Mass Action, the concentration of $\text{Fe}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$ will be diminished in favour of more $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$. It seems likely that the former is more redox-active than the latter, both thermodynamically and kinetically (§11.8), with the result that the coated paper and sensitizer solution may have a longer shelf-life, because they are less susceptible to reducing agents; it is also possible that the contrast may be increased thereby.

The 'traditional' platinotype sensitizers (§6.3) on the other hand, use ferric oxalate (§11.2) in which the iron:oxalate ratio is 2:3. Since the coordination number of Fe(III) when surrounded by oxygen-donor ligands is usually not less than 6 (and may be 7) then there must be water molecules, hydroxo-, or oxo-ligands in the Fe(III) coordination spheres of the ferrioxalate species in solution, such as $\text{Fe}(\text{C}_2\text{O}_4)_2(\text{OH}_2)_2^-$ and $\text{Fe}(\text{C}_2\text{O}_4)(\text{OH}_2)_2(\text{OH})_2^-$. These provide a facile route for oligomerization via -OH bridging groups, forming initially dimers of the sort

$\text{Fe}_2(\text{C}_2\text{O}_4)_4(\text{OH}_2)^{2-}$ (a common structure for Fe(III) see §10.2), but then further polymerization, possibly via oxalate bridges,⁷⁴⁰ is also possible. In view of the recently elucidated highly polymeric layer structure of solid ferric oxalate (see §11.2), the molecular structures of the species in ferric oxalate solution are most probably oligomeric, variable, and bridged by oxalate ligands. These structures are unknown, apart from the fact that Mössbauer spectroscopy has indicated a slightly distorted octahedral FeO_6 primary coordination sphere (see §11.2) as expected.

The addition of excess oxalic acid to the ferric oxalate sensitizer solution, which is generally recommended, likewise affects the coordination sphere, by displacing water or OH^- ligands, in favour of forming $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$:



This reaction could affect the photochemical behaviour: more oxalate causes a greater degree of print-out versus development, lessening the possibility of reversal, and improving the ease of clearing, by diminishing the coordination of Fe(III) to cellulose. Thus, in the 'standard' traditional 25% w/v ferric oxalate solution (see §6.3) there is usually included ~2% w/v of additional oxalic acid, which is sufficient to convert ~10% of the ferric oxalate to the complex anion trisoxalatoferrate(III): *i.e.* providing ~10% print-out. However, some workers are reputed to add as much as 15% to 18% w/v of oxalic acid to their ferric oxalate solution, which would result in conversion of ~90% of it to potentially printing-out trisoxalatoferrate(III) anion.⁷⁴¹

10.6 Solubility of potassium ferrioxalate

Employing the trisoxalatoferrate anion in sensitizer solutions has one drawback: it cannot be used in a mixture containing a high concentration of potassium cations [K^+] because the salt, potassium ferric oxalate, ($\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$ FW 491.26) has a relatively low solubility and may crystallise out, which would spell disaster for the paper coating operation. This problem does not arise with the traditional sensitizer using potassium tetrachloroplatinate because the ferric oxalate solution presumably contains only a small proportion of $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ at equilibrium, if any. In the Malde-Ware printout sensitizer, however, with pure ammonium trisoxalatoferrate, potassium tetrachloroplatinate cannot be used and must be replaced by the ammonium or sodium salt, or in the similar Ziatype process, by the lithium palladium salt.

It is possible to quantify this problem from the known solubility of the potassium salt; it is reported that:

100 cc of water dissolve 4.7 g $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$ at 0°C	
6.6 g	at 15°C
117.7 g	at 100°C

so by a rough interpolation ~10 g at ~20°C

This last figure gives us a working saturated solution at room temperature as ~0.2 molar. From this concentration, it is possible to calculate the solubility product (assuming 'ideal' solution behaviour):⁷⁴²

$$K_{sp} = [\text{K}^+]^3 [\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}] = 27 \times 0.2^4 = 0.0432 \text{ at } 20^\circ\text{C}$$

and thence predict the potassium ion concentrations that will just cause the onset of crystallization for a given ferrioxalate concentration, as follows:

[Fe(C ₂ O ₄) ₃ ³⁻]	[K ⁺] for crystallization
0.1 molar	0.756 molar
0.2	0.600
0.3	0.524
0.4	0.476
0.5	0.442
0.6	0.416
0.7	0.395

If one assumes that the stoichiometric molar ratio Fe : Pt = 2 : 1 applies in the mixed solution, then the relationship $[K^+] = [Fe(C_2O_4)_3^{3-}]$ holds, whence $[Fe(C_2O_4)_3^{3-}] = 0.456$ molar is found to be the critical limiting concentration that can be used, with potassium as cation. The Willis method uses an iron concentration (0.515 molar) in excess of this, but the substance is ferric oxalate, which contains little or no $Fe(C_2O_4)_3^{3-}$ ions. The Malde-Ware method uses $[Fe(C_2O_4)_3^{3-}] = 0.7$ molar, but avoids K^+ entirely, substituting it with NH_4^+ .

10.7 Photochemical effects on iron(III) speciation

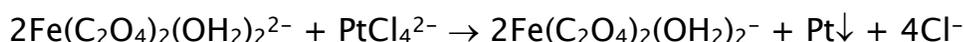
In the unexposed and highlight regions of an exposed but unprocessed Pt/Pd print, the Fe(III) species will be predominantly the same as in the unaltered ferric oxalate sensitizer – soluble in water and not too extensively hydrolysed – which should therefore be quite readily removed in the clearing process. However, in the heavily exposed shadow regions of the print, effectively all the Fe(III) species will have lost some of their coordinated oxalate ligands, due to the photochemical oxidation of $C_2O_4^{2-}$ to $2CO_2$ e.g. stoichiometrically:



The iron(II) oxalate photoproduct is insoluble, having a polymeric linear chain structure (§11.2) and cannot react with the Pt(II) or Pd(II) salt until it is solubilised by complexation with the oxalate:



whereupon the iron(II) complex can reduce the platinum metal salt to precipitate the metal, being itself re-oxidized to Fe(III):



The precise Fe(III) species formed after exposure will depend on the conditions of development: some of the resulting Fe(III) species may end up with more water in the coordination sphere, and become more liable to hydrolysis,

and more difficult to clear from the shadow areas. However it will also be effectively invisible there, to the naked eye, due to the high optical density. This offers an explanation for Chapman Jones' observation (see §9.1) of more iron retained in the shadows. The effectiveness of clearing is usually judged by the absence of obvious discoloration in the highlights of a print. The possibility of even greater contamination in the shadows is not generally considered. So we will also need to test the shadow tones for Fe(III) lurking unseen in their depths, by examining the UV spectra for LMCT peaks at *ca.* 300 nm, and the XRF spectra for presence of Fe. Fe(III) is likely to generate acid by hydrolysis (see §10.2) so Fe(III) and/or H⁺ may slowly diffuse out of the shadow regions of a print, depending on the prevailing RH and temperature, and eventually become conspicuous in the adjacent highlight regions as a "halo stain", which has been observed in some platinum–palladium prints.

10.8 Staining of cellulose by iron(III)

There is a long-standing historical precedent for the knowledge of the retention of iron salts by cellulose, to be found in the practices of calico-printing, where residual iron was actually encouraged as a mordant for the dyestuffs. In 1859 George Wilson was drawing the attention of the Photographic Society to:

"...a well-known process in calico-printing called "aging," which consists in exposing to the air cottons charged with salts of iron or alumina, till these are chemically altered and combined with the textile tissue. The aging has hitherto occupied a week or thereabouts; but Mr Walter Crum, of Glasgow, who is as remarkable for his knowledge of chemical science as for his ingenuity and success in applying it to practice, recently showed me the process of aging completed in one day. This striking acceleration of chemical change is brought about simply by substituting hot moist air for that which was cold and dry. Conversely, coldness adds to dryness and darkness an additional element of conservation."⁷⁴³

Evidently, George Wilson and Walter Crum deserve to be considered as the first photograph conservators, and Crum might also be acclaimed as the inventor of the technique of "accelerated ageing"!

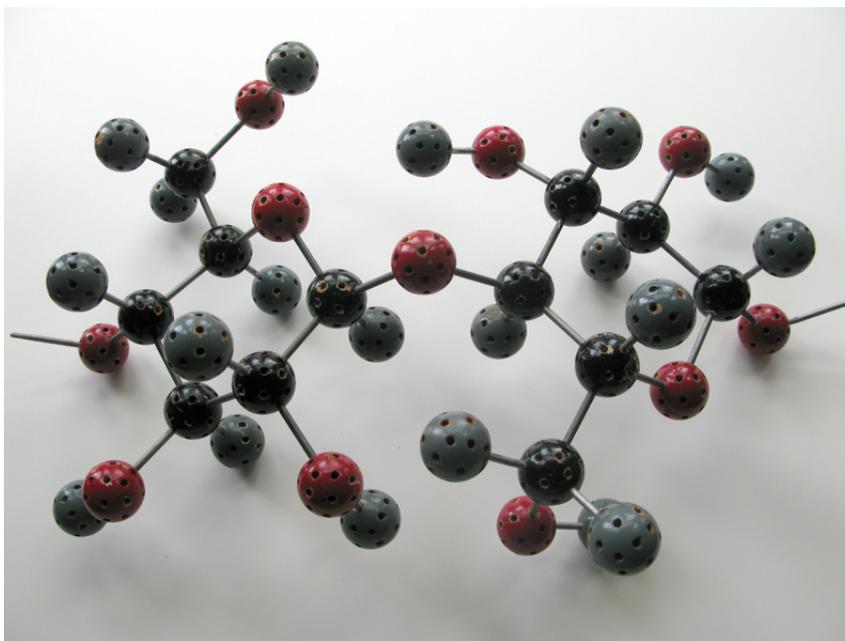


Fig. 10.2 Double glucopyranose repeat unit of the cellulose chain

Once our siderotype sensitizer is applied to paper, we have an additional ligand to consider – the cellulose itself. It is a linear β -1,4 linked polymer of the monosaccharide β -D-glucopyranose: $(C_6H_{10}O_5)_n$ where $n \sim 15,000$, see Fig. 10.2.

The cellulose molecule is potentially a chelating ligand towards iron(III) and will compete with the other ligands in the coordination sphere, which may initially be attracted to the cellulose by hydrogen-bonding.



Fig. 10.3 'FeO₆' coordinated to vicinal -OH groups in cellulose

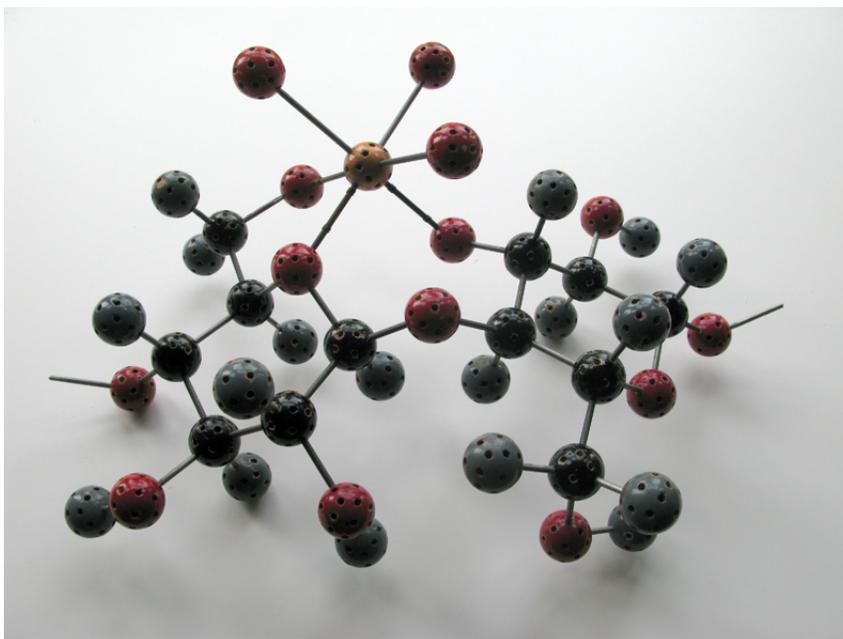


Fig. 10.4 'FeO₆' coordinated to -O- and 2 -OH groups in cellulose

Ligand replacement by cellulose would account for the very strong binding of Fe(III) to paper, and the problems of persistent yellow staining in platinotypes and palladiotypes. In each monomer unit there are two pairs of vicinal -OH groups that could coordinate sterically to an Fe(III) centre to form a cis-bidentate complex, probably octahedral, as shown in Fig. 10.3. There is also the steric possibility of cellulose acting as a facially terdentate ligand towards iron, using as donor atoms the ring ether oxygen and one hydroxyl from each adjacent glucose unit, see Fig. 10.4.

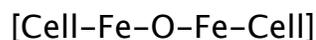
Although the coordination shown in Figs. 10.3 and 10.4 is entirely conjectural, there is good evidence that the binding of Fe(III) to cellulose can be strong,⁷⁴⁴ so much so that it has recently been developed as a method for permanently dyeing cellulose fibres,⁷⁴⁵ and has long been known in the practices of calico-printing, as mentioned above. The complexes iron(III) succrate and iron(III) glucosate may serve as models for the binding of Fe(III) to cellulose.

This hypothesis could be probed spectroscopically for further evidence of coordination of the Fe(III) to glycosidic -O- and -OH groups in the stained regions of papers. It should also be borne in mind that in alum-rosin sized papers the Al³⁺ ions may also bind strongly to the cellulose and compete with Fe³⁺ at these coordination sites. This may be the reason why alum-rosin sized papers like Weston Diploma Parchment and Cranes are observed to have less tendency to iron-staining than 'modern' papers.

The likely presence of chemisorbed Fe(III) in cellulose offers a possible explanation for the slow appearance of the yellow staining referred to in §9.2. The Fe(III) starts out with a monomeric structure, with six oxygen donor ligands usually, such as OH, OH₂, or HOC-. The [Fe^{III}O₆] chromophore is only weakly absorbing of visible light: the Ligand-to-Metal Charge Transfer (LMCT) absorption band lies in the UV with little tail into the visible; the d-d transitions

of octahedral Fe(III), which is d^5 high spin, fall in the visible region but are all spin-forbidden and therefore very weak in the simple aqua-cation.

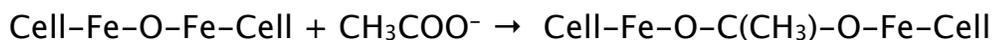
However, with time it is possible that [Cellulose-FeOH] units on adjacent cellulose chains could associate by eliminating H_2O and cross-linking to form a binuclear μ_2 -monooxodiiron(III) species, which we will simply represent by



This reaction would probably be promoted by heat, but it is not obvious how it would depend on RH and pH. The $[\text{O}_5\text{Fe-O-FeO}_5]$ chromophore absorbs strongly in the visible region due to Metal-to-Metal Charge Transfer (MMCT), mediated by antiferromagnetic superexchange between the linked Fe(III) centres through the π orbitals they form with the bridging μ -oxo group. The molar absorptivity in the visible region is consequently much higher, causing a brown colour (§10.2) which is very evident in model compounds.⁷⁴⁶ Treatment with H_2O/H^+ could split the dimer and reform monomeric Fe(III):



or a bridging ligand such as acetate could spread the iron(III) centres apart:



again greatly diminishing the colour intensity but not removing the Fe(III). XRF analysis shows that although the colour is bleached by treatment with acetate, the iron is not removed. If reversible, this would explain the long-term outcome of Steichen's treatment of Stieglitz's palladiotypes which have re-yellowed.

Cellulose microfibrils may also physically trap FeO(OH) or Fe_2O_3 if nanoparticles of these ultimate products of the hydrolysis reactions are formed in regions of discoloration, it may be possible to detect these particles by electron microscopy. The UV-visible spectrum and magnetism may also provide clues to their presence.

10.9 Chelation of iron

It has long been known that multidentate ligands (chelates) can bind metal cations, including iron, much more effectively than can simple monodentate ligands. The best known of these chelating agents is EDTA, ethylenediaminetetraacetic acid, (aka 1,2-diaminoethanetetraethanoic acid). It is usually employed as one of its water-soluble sodium salts. The four successive acid dissociation constants for the tetrabasic acid, $H_4\text{EDTA}$ have pK_a values:⁷⁴⁷

$$pK_1 = 2.0; pK_2 = 2.7; pK_3 = 6.2; pK_4 = 10.3.$$

It follows that solutions of the mono- and di-sodium salts are mildly acidic, pH 3~4; a solution of the trisodium salt is about neutral, pH ~7; and a solution of the tetrasodium salt is quite alkaline, pH 9~10. The ligand has four carboxylato and two tertiary amino groups, Fig. 10.5:

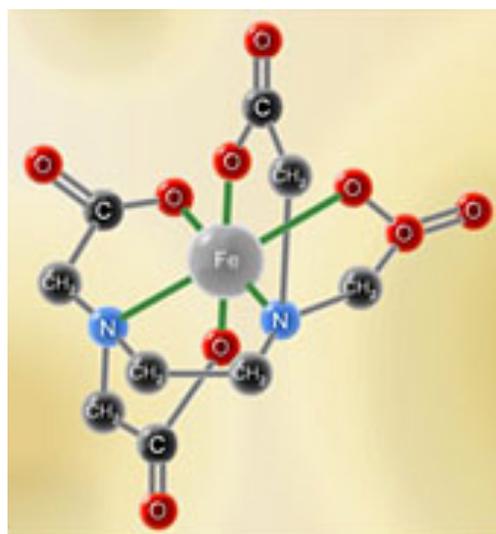
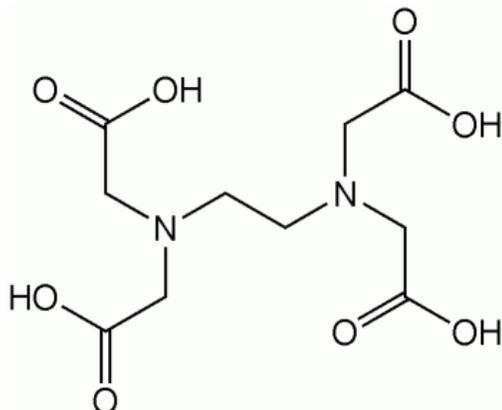


Fig. 10.5 The structure of EDTA and 10.6 the Iron(III) EDTA complex

This molecule can act in a hexadentate manner, wrapping itself around the six coordination sites of an octahedron without incurring much strain, Fig. 10.6: The formation constant for the iron(III) complex $K_f = 10^{25}$.

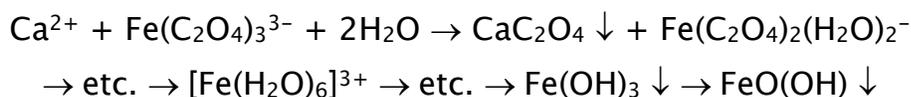
There are several analogues of EDTA, such as:

- CDTA (cyclohexanediaminetetraacetic acid) and
 - HBED (N,N-bis(2-hydroxybenzyl)ethylenediamine-N,N-diacetic acid),
 - DTPA (diethylenetriaminepentaacetic acid),
- which have even larger formation constants for their Fe(III) complexes.

10.10 Chemistry of clearing siderotypes

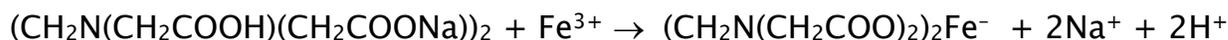
Once the noble metal image has been fully formed within the paper fibres, it only remains to remove completely the excess chemicals – sensitizer and reaction products – to reach a stable image. The process of development and clearing described in Chapter 7 has been evolved to achieve this most thoroughly and expeditiously. Lest it should be thought that the choices for this procedure are arbitrary, their chemical logic will be explained here.

The exposed and printed-out sensitizer layer will contain, in addition to the nanoparticle noble metal image, the following ions: aquated iron(III) oxalato complexes, free oxalate anion, ammonium or potassium cations, tetrachloroplatinate or tetrachloropalladate anions, and chloride ions. Most of these are soluble in water and will be easily removed in the washing. The chief problem for effective clearing is the iron(III), some of which may bind chemically to the hydroxylic functions of the cellulose, *i.e.* it may be ‘chemisorbed’. Moreover, at pH values above 4, iron(III) tends to hydrolyse, as described in §10.3, forming polymeric colloidal iron(III) hydroxide, which could lodge in the paper fibres and eventually impart a yellow stain. In addition, any calcium ions in the washing water (‘hardness’) or in the paper (chalk buffer) will tend to precipitate insoluble calcium oxalate, and promote aquation and hydrolysis of the Fe(III) complex:



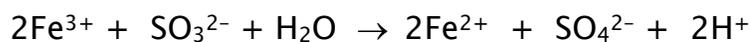
While freshly-formed iron(III) hydroxide can be redissolved in dilute acids initially, if it is not soon removed it slowly transforms irreversibly, as described above in §10.3, into a highly insoluble polymeric form, iron(III) oxyhydroxide, FeO(OH) – the mineral called Goethite – which is quite insoluble in dilute acids. It is therefore essential to remove all the iron(III) at the wet processing stage before the print dries, and this is achieved with the following clearing sequence, as described practically in §7.22:

1. A bath of disodium EDTA *ca.* 5% *w/v* (*ca.* 0.14 M), which is acidic at pH 3–4, suppresses hydrolysis, chelates iron(III) well, see §10.9, and removes most of it:



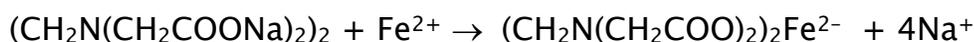
N.B. It is important **not** to use tetrasodium EDTA for the *first* processing bath – In spite of the fact that it has been recommended by Bostick & Sullivan – it has a high pH ~10 at which the iron(III) is not effectively complexed, but rather hydrolysed, with the eventual result of yellow or brown staining.

2. A bath of sodium sulphite (Na₂SO₃) or disulphite (Na₂S₂O₅) *ca.* 2.5% *w/v* is made up fresh for each printing session because it does not keep, being oxidised by air to sulphate. This bath is intended to reduce any residual iron(III) still bound to the cellulose to iron(II), as described in §9.6:



The reduction product, iron(II), is less strongly bound to cellulose and less extensively hydrolysed than iron(III), so is more easily and completely removed in the final chelating bath that follows.

3. A bath of tetrasodium EDTA *ca.* 5% *w/v*, which is alkaline at pH 9–10, the optimum pH for chelating residual iron(II), removes the last traces of iron and leaves the paper sheet in an alkaline condition, which is desirable for its preservation:



This tetrasodium EDTA bath, after the sulphite reduction bath, has a long life, because there is so little iron left in the prints by the time they reach it; most comes out in the first bath. It is changed when discoloration begins to be apparent.

This clearing method has been tested and compared with other clearing procedures by XRF analysis of the residual iron in a platinum or palladium print. Matthew Clarke and Dana Hemmenway found this procedure to be the most effective of all they tested, leaving the iron level lower than any other combination of clearing agents, and of an iron concentration comparable with, or even less than, the original iron content of the uncoated paper.⁷⁴⁸ Accelerated ageing tests of the cleared papers did not produce any perceptible yellow stain.

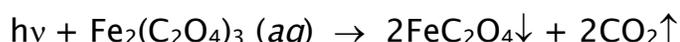
In cases where the advice above has not been followed, resulting in yellow stains eventually appearing in the highlights of a finished print, a more energetic clearing procedure using the powerful reductant sodium dithionite, may remove the stain, as described in §9.5.

11. Chemistry of Platinum and Palladium Printing

The characteristics – and some of the difficulties – of platinum printing arise from the relative slowness of the chemical reactions of platinum complexes. Palladium, by contrast, affords much speedier reactions; the greater vigour of its chemistry largely accounts for the differences between the two noble metals when used for photographic printing.

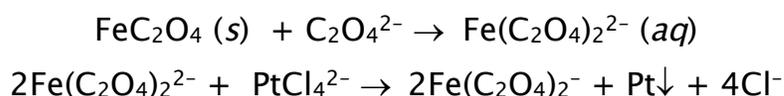
11.1 Photochemistry of iron(III) oxalates

The platinotype and palladiotype are 'iron-based' or *siderotype* processes in which the photosensitive material is an oxalato-complex of iron(III), traditionally ferric oxalate itself.⁷⁴⁹ Döbereiner in 1831 was the first to observe the light-induced decomposition of iron(III) oxalate in aqueous solution (see §1.6).⁷⁵⁰ The reaction results in the evolution of carbon dioxide gas and the precipitation of the insoluble salt ferrous oxalate:



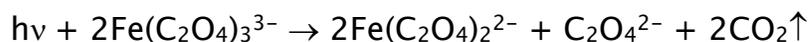
Photosensitivity has also since been discovered in other carboxylates of iron(III), notably the citrate, malonate, tartrate and glycollate complexes; although no clear criterion has yet emerged for deciding what structural feature of such complexes is necessary for photosensitivity. Balzani and Carassiti have proposed a mechanism for the photochemistry of α -hydroxycarboxylato-iron(III) salts, involving intramolecular electron transfer from the coordinated anion to iron(III), reducing it to iron(II); the radical formed in the primary process then reduces an unexcited complex, and the ligand thereby undergoes oxidative decarboxylation.⁷⁵¹

The photoproduct from iron(III) oxalate is the fairly insoluble iron(II) oxalate, FeC_2O_4 (solubility: 0.022 g/100 cc water) which cannot reduce platinum(II) or palladium(II) salts in aqueous solution to the metal unless it is solubilised by complexation, e.g. with oxalate ions:



Hence the development process of platinum and palladium printing, which calls for a processing bath of concentrated potassium oxalate solution, sometimes also containing a ligand such as phosphate.

The alternative photosensitive iron(III) salt for platinotype is ammonium or sodium iron(III) oxalate, which contain the well-characterised complex ion, trisoxalatoferrate(III). A 3D model of this ion may be enjoyed here.⁷⁵² This undergoes a similar photochemically-induced redox reaction, yielding carbon dioxide and a soluble oxalato-complex of iron(II). The overall stoichiometry can be represented by:

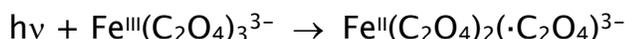


It is evident from the standard redox potentials⁷⁵³ that this reaction should proceed spontaneously:

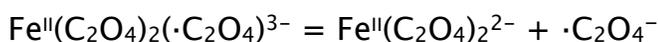
$$E(\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}/\text{Fe}(\text{C}_2\text{O}_4)_2^{2-}) = +0.02 \text{ V}$$

$$E(2\text{CO}_2/\text{C}_2\text{O}_4^{2-}) = -0.49 \text{ V}$$

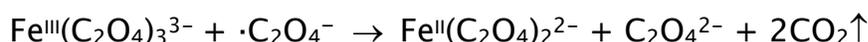
but at ambient temperature there is a kinetic barrier to this process which is only overcome when the complex is photoexcited by absorption of ultra-violet light in the vicinity of its ligand-to-metal charge transfer band at $\lambda_{\text{max}} = 260$ nm. This reaction has been the subject of much photochemical investigation;⁷⁵⁴ a mechanism for the photolysis in aqueous solution was first suggested by Hatchard and Parker;⁷⁵⁵ it proceeds from the initial formation of a radical anion by electron transfer from one oxalate ligand to the iron(III), reducing it to iron(II):



The ligand radical anion will be in dissociative equilibrium with the complex:



Reaction of the radical anion, $\cdot\text{C}_2\text{O}_4^-$, or even its partially coordinated complex, with a further molecule of the original iron(III) complex enables the transfer of the second electron from the ligand, which is then lost as two molecules of carbon dioxide, leaving another mole of the iron(II) oxalato complex:



The quantum yield for ferrioxalate photoreduction in this process should ideally be $\phi = 2$; but the competing reverse dark reaction tends to diminish this. The measured quantum yield per mole of iron(II) formed in aqueous solution is approximately 1.2 for radiation of wavelengths between 250 and 420 nm, falling slightly to 0.9 at 500 nm, but very sharply thereafter – see §12.3.⁷⁵⁶ The quantum yield is found to be largely independent of pH. Under acidic conditions, *ca.* pH 2, the colour of a solution of trisoxalatoferate(III) changes from emerald green to light yellow, corresponding to the formation, as the predominant species, of the hydrated complex ion $\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$ which may be isolated as a crystalline solid with suitable large cations; it is still light-sensitive with approximately the same quantum yield.⁷⁵⁷

11.2 Ferric oxalate versus ammonium ferric oxalate

The ills of the traditional development platinotype method stem from the choice of ferric oxalate as the photosensitive iron(III) salt, as described in §6.2. This is historically a notoriously wayward and ill-characterised substance, which is polymeric and capable of extensive polymorphism, the product varying with its method of preparation. Its formula is variously said to contain 4, 5, or 6 molecules of lattice water. An indicator of the difficulty of manufacture is evident from its commercial price: iron(III) oxalate often costs over 100 times as much as iron(II) oxalate! Unsurprisingly, there are few suppliers of this chemical, because it has no entry in the Fine Chemicals Data Base, and a certain mystique has been claimed to surround its preparation and properties.⁷⁵⁸

Infrared and Raman spectra of the hexahydrate show that it does not contain any free oxalate anion or trisoxalatoferrate(III) ions, and that the molecule is probably non-centrosymmetric.⁷⁵⁹ Recent Mössbauer spectroscopy shows that the Fe(III) centres are all similar in electronic environment, and high spin, and have a nearly regular octahedral FeO₆ coordination sphere.⁷⁶⁰ Ferric oxalate seems to be uncrystallizable, and has not therefore had its structure determined by single crystal X-ray diffraction; but very recently in 2015 one relatively well-characterised form of the solid, analysing as the tetrahydrate, Fe₂(C₂O₄)₃·4H₂O, was studied by powder X-ray and neutron diffraction and the structural parameters for the unit cell were obtained.⁷⁶¹ The structure is polymeric, composed of zig-zag chains in which the octahedral Fe(III) centres are bridged by cis-bidentate oxalate ligands, and these chains are cross-linked into a 2-dimensional layer structure by the third trans-bis-monodentate oxalate ligand; each Fe(III) centre also carries one coordinated water molecule to complete its octahedral coordination sphere. The two remaining lattice water molecules are hydrogen-bonded within the unit cell. By comparison, the oxalate ligands in ferrous oxalate dihydrate are trans-bidentate, giving rise to linear chains.

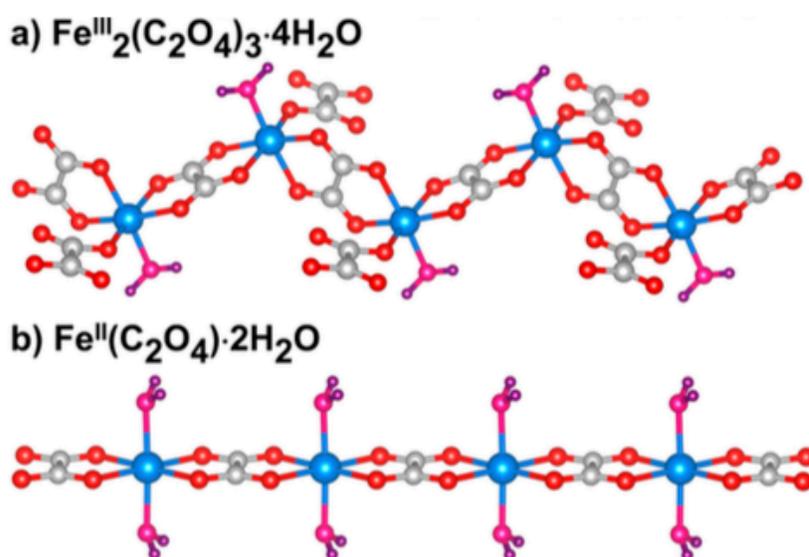


Figure 9. Comparison between iron coordination in humboldtine ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) and $\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$. The color code used is the same as in Figure 2.

Fig. 11.1 Structures of ferrous and ferric oxalate

We can now understand from this highly polymeric structure why ferric oxalate is very slow to dissolve in water without the aid of additional ligands, and why its aqueous solution may change properties over time, to the extent that some scrupulous platinotypists prefer to make up a fresh solution the night before every printing session.⁷⁶² It is not yet known what the molecularity of the solution species is, but it is likely to consist of a complex mixture of oligomers, highly temperature-dependent and slow to reach equilibrium.

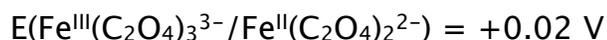
In the author's work over the last 30 years it has been found advantageous to avoid the ill-defined iron(III) oxalate, and use instead the well-characterised ammonium iron(III) oxalate, (§10.5) which is a highly crystalline pure substance of known molecular structure, $(\text{NH}_4)_3\text{Fe}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$, FW 428.07, containing the monomeric anion $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$. It is universally available at low cost, and dissolves very readily to give a concentrated aqueous solution, approximately 1.4 molar at saturation, which is stable for years in the dark, see §7.6.⁷⁶³ Moreover, the photochemistry leads to a print-out process, as was first observed with sodium iron(III) oxalate by Giuseppe Pizzighelli in 1887 – see §1.16 & §5.3 – which has a number of practical advantages, as described in §7. The only precaution that need be taken is to avoid a high concentration of potassium ions in the sensitizer, for solubility reasons explained in §10.6.

The explanation for this difference in behaviour is that the iron(II) photoproduct in the case of trisoxalatoferate(III) anion is already a soluble complex ion, as we have seen in §11.1 above, so if the sensitized paper contains a sufficiency of water molecules, as will be the case for any cellulose paper exposed to an ambient relative humidity of 70–80%, the ions can migrate to reduce the platinum(II) to Pt metal *in situ*. Thus a print-out process results, in which the final image is substantially formed during the light exposure, and no development bath is required, simply clearing baths to remove the excess soluble chemicals. This enables a *modus operandi* quite different from the traditional method: it is more economical of time, effort, and materials. Images may be printed satisfactorily by inspection, without prior calibration by test strips.⁷⁶⁴ The print-out process is self-masking in that the blackening of the shadow tones during the exposure partially inhibits their further darkening, so a longer density range in the negative may be accommodated in the print without total loss of detail simply by extending the exposure time. The consequence is that a wider range of negatives become printable without the rigorous control of contrast that is typically exercised in the development process.

A further benefit of the use of the ammonium iron(III) oxalate print-out sensitizer appears to be that it is immune from the "plague of black spots" that sometimes afflicts the iron(III) oxalate development process, as described in §9.11.⁷⁶⁵ This may be connected with the solubility of the reduction product.

11.3 Siderotype by reduction of noble metals

The iron(II) oxalato-complex formed photochemically is a moderate reducing agent, as indicated in §10.5 by its redox potential:



In the event that the system is chelated by EDTA, used as a clearing agent, the Fe(III)/Fe(II) couple is even more strongly reducing:



so either of these couples suffices to reduce compounds of metals having more positive potentials, yielding the metal itself, which constitutes the final image. We note in passing that the redox potential of the citrato-complex of iron(II):⁷⁶⁶

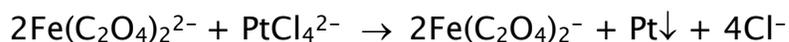


shows it to be a weaker reducing agent than the oxalato-complex (compare the value of +0.02 V, above), and it does not reduce platinum(II) or palladium(II), although it will reduce gold(III) and silver(I), under the printing conditions. The ease of reduction is reflected in the relative values of the redox potentials:

Metal	Couple	Redox potential
platinum	$E(\text{PtCl}_4^{2-}/\text{Pt},4\text{Cl}^-)$	+0.73 V
	$E(\text{PtBr}_4^{2-}/\text{Pt},4\text{Br}^-)$	+0.68 V
palladium	$E(\text{PdCl}_4^{2-}/\text{Pd},4\text{Cl}^-)$	+0.62 V
	$E(\text{PdBr}_4^{2-}/\text{Pd},4\text{Br}^-)$	+0.60 V
silver	$E^\circ(\text{Ag}^+/\text{Ag})$	+0.80 V
gold	$E(\text{AuCl}_4^-/\text{Au},4\text{Cl}^-)$	+1.00 V
	$E(\text{AuBr}_4^-/\text{Au},4\text{Br}^-)$	+0.87 V
mercury	$E^\circ(\text{Hg}^{2+}/\text{Hg})$	+0.85 V

Table 11.1 Redox potentials of "noble" metals

Such metals that are hard to oxidise belong to the category once designated as "noble" (§1.1); conversely, their salts are readily reducible. In the case of platinum, for example, the reaction is:



where the iron(III) oxidation product $\text{Fe}(\text{C}_2\text{O}_4)_2^-$ will subsequently coordinate more ligands, such as $\text{C}_2\text{O}_4^{2-}$ or H_2O . Similar equations can be written for the other metals. However, kinetic factors may make the rates of such reduction reactions too slow to be useful unless the noble metal complex is sufficiently labile, (as are all those cited above). For instance, the chemical thermodynamics also permits the reduction of hexachloroplatinate(IV) anion:

$$E(\text{PtCl}_6^{2-}/\text{Pt},6\text{Cl}^-) = +0.68 \text{ V}$$

but this complex is too inert kinetically to yield a platinum image within the short time of a few minutes that is available for the reaction to take place. Prolonging the reaction time excessively will only result in re-oxidation of the iron(II) photoproduct back to iron(III) by the air. The same was also found by the author to be true experimentally of $\text{Pt}(\text{NH}_3)_4^{2+}$, $\text{Pt}(\text{NO}_2)_4^{2-}$, $\text{Pd}(\text{NH}_3)_4^{2+}$, RuCl_6^{2-} , IrCl_6^{3-} , and RhCl_6^{3-} , for which ferrioxalate sensitizer produced no images.⁷⁶⁷

The various processes used historically to make siderotypes are summarised in Table 11.2, together with their authors, the approximate year of their invention, the nature of the iron salt used and the image substance. A distinction is made between those processes that employ ferric oxalate, and those that use trisoxalatoferrate(III) as sensitizer.

Year	Inventor	Process Name	Iron Salt	Image substance
1842	Herschel	Cyanotype	Citrate	Prussian blue
1842	Herschel	Argentotype	Citrate	Silver
1842	Herschel	Chrysotype	Citrate	Gold
1842	Herschel	Kelainotype	Tartrate	Mercury
1858	Mercer	Chromatic Photograph	Oxalate	Vegetable dyes
1859	Poitevin	Ferrogallate	Tartrate	Iron(III) gallate ink
1861	Phipson	Phipson's process	Oxalato-	Manganese dioxide
1864	Obernetter	Ferro-cupric process	Chloride	Copper ferrocyanide
1873	Willis	Platinotype	Oxalate	Platinum
1877	Pellet	Pellet print	Tartrate	Prussian blue
1878	Willis	Sepia Platinotype	Oxalate	Platinum+Mercury
1887	Pizzighelli	Direct Print Platinotype	Oxalato-	Platinum
1889	Nicol	Kallitype	Oxalate	Silver
1889	Shawcross	Sepiatype	Citrate	Silver
1889	Arndt	Vandyke	Citrate	Silver
1895	Nakahara	Ferrogallate	Tartrate	Iron(III) gallate ink
1897	Jarman	Aurotype	Citrate	Gold
1913	Willis	Satista	Oxalate	Platinum+Silver
1917	Willis	Palladiotype	Oxalate	Palladium
1987	Ware	New Chrysotype	Oxalato-	Gold
1991	Ware	Argyrotypes	Citrate	Silver
1994	Ware	New Cyanotype	Oxalato-	Prussian blue

Table 11.2 Siderotype Processes
(Oxalato- denotes use of ammonium or sodium trisoxalatoferrate(III))

11.4 Printing in palladium and platinum compared

The contemporary platinum–palladium practice at the opening of the 21st Century attests that it is very much easier and less expensive to print successfully in palladium than it is in platinum. Very few practitioners today even attempt the latter, most preferring either to use palladium entirely, or to compromise with a mixture of the two metals in which palladium predominates. This is also the stated preference of the leading retailer of palladium and platinum printing kits and chemicals in the USA.⁷⁶⁸ The current difficulties with platinum printing are attributed by some to changes in the manufacture of fine paper, and in the present climate there is an impression that palladium printers are "making a virtue of necessity".

Chemically speaking, we can say that the disparity between the performance of the two metals may be attributed to the higher reactivity of the complexes of palladium(II) compared with those of platinum(II), as would be expected for a second–row (4d), contrasted with a third–row (5d) transition metal. In the sequential building–up of the electronic structures of atoms, the *Aufbauprinzip* of Niels Bohr, there is an effect known as the 'lanthanide contraction',⁷⁶⁹ which is responsible for the fact that, despite their widely differing atomic numbers, the two elements palladium and platinum are about the same size, both as atoms in the metallic state and as their 2+ and 4+ cations as shown in Table 11.3.⁷⁷⁰

Atomic Property	Coordination No.	Palladium	Platinum
Atomic Number Z		46	78
Relative Atomic Mass A		106.4	195.1
Metallic radius in pm	12 (cubeoctahedral)	137.3	138.5
r(M ²⁺) (Shannon & Prewitt)	4 (square planar)	78	74
r(M ⁴⁺) "	6 (octahedral)	75.5	76.5
First Ionization energy in kJ/mol		804	865
Second Ionization energy		1874	1791
Density of fcc metal in g/cc		12.0	21.45

Table 11.3 Comparative properties of palladium and platinum atoms/ions

As a consequence, although the two metals resemble one another in their structural chemistry, platinum is more electron–dense than palladium, and the effective nuclear charge experienced by bonding electrons in its valence orbitals, 6s and 6p, will be higher, conferring stronger binding energies on its complexes than those of palladium.

The reaction kinetics of complexes of a third row transition metal like platinum are generally slower than those of a second row metal like palladium, due to larger ligand field activation energies, resulting from the greater spatial extent of the 5d-orbitals. Thus the more labile palladium(II) complexes are easily and rapidly reduced to the metal by the iron(II) photoproduct. The rapidity of this reaction may also account for the greater tendency of palladium printed by development to suffer reversal and a dichroic image (§6.18): nanoparticles formed more rapidly in the shadow areas will be smaller and therefore warmer in colour. By contrast, platinum complexes are slower to react and the images are not known to suffer reversal. Their reduction to the metal may be further inhibited by various impurities or additives in the paper, such as gelatin, some varieties of which can bind strongly and irreversibly to platinum(II) as discussed in the next section.⁷⁷¹

If the wet processing washes the soluble platinum salts out of the paper before they have had opportunity to react fully with the iron(II) photoproduct, the image will appear weak and fibrous or grainy. This problem with Platinotype was recognised 130 years ago by Willis. He also discovered that certain substances can accelerate the response of the platinum chemistry, notably the salts of mercury(II) and lead(II). As we have seen in §6, these were used as additives in the formulations by Willis and others seeking to improve the Platinotype process, but they are unnecessary in the Palladiotype process, which readily gives a smooth result on a wider range of papers with a simple sensitizer formulation, without addition of lead or mercury salts. The palladium image is also usually warmer in tone and may readily be obtained in a sepia colour, depending on the RH, making the addition of mercury salts unnecessary for that purpose. Indeed, the effect of mercury(II) has been shown to be a distinct cooling of the brown palladium image.⁷⁷² The susceptibility of palladium to be dissolved by dilute hydrochloric acid noted in §2.8 can only be understood if the oxygen of the air:



is also involved in supplying the necessary oxidising power (cf. Table 11.1).

Printing of a mixture of platinum and palladium in any proportion is facilitated by the fact that the two metals form a continuous solid solution over whole range of composition, as is seen in the binary phase diagram for Pt/Pd. The platinum and palladium sensitizer solutions described in §7 may be mixed in any proportion, provided that their total volume approximately equals that of the iron(III) solution. Such a sensitizer consisting of a mixture of these will not in general produce an image having the two metals in the same original proportions, as a consequence of the disparate rates of the reduction reactions of platinum(II) and palladium(II). Many contemporary so-called "platinum-palladium prints" must, in fact, consist chiefly of the latter metal, the greater part of the platinum salt used in their making having been washed away in the wet processing before it had time to react fully, as has recently been visually demonstrated by a leading practitioner.⁷⁷³ This is also the reason why 100% platinum prints are difficult to make. Inhibition of this washing out by raising

the viscosity of the developer is the basis for the "glycerine method" of development, first described by Willis, and by Stieglitz and Keiley (§3.3).

The technical evaluation of mixed platinum/palladium printing requires quantitative analysis of the image metals present in each individual print. The resulting image will consist of a mixture of the two metals but not in the same proportion as the sensitizing solution, because palladium 'prints out' about 2.5 times faster than platinum (in the middle tones) on many papers. This has been demonstrated by quantitative analysis by X-ray fluorescence spectrometry (XRF) of coated papers, both before and after exposure and processing, as follows.⁷⁷⁴

A mixed sensitizer solution, having a molar ratio of Pt:Pd = 1:1 was used. Before exposure, the XRF analysis of the coating agreed with the proportion in the bulk sensitizer; after exposure and processing the ratio of each metal to the total was found to vary with the exposure time in the manner shown in Fig. 11.2, where the proportion of palladium in the image is always seen to be higher than platinum, with Pt:Pd = 1:3 initially for low exposures, and levelling off around 3:4 for maximum exposures.

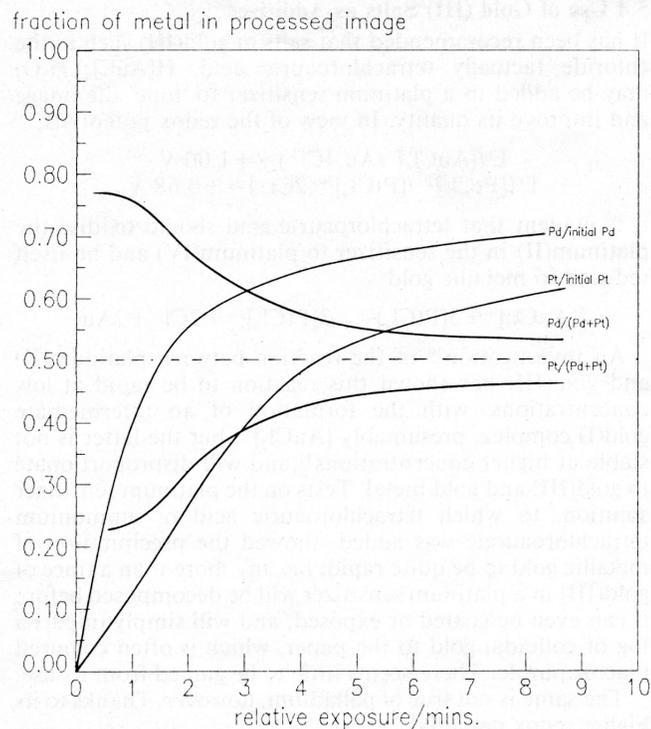


Fig. 11.2 Deposition of Pt and Pd from a mixed sensitizer Pt:Pd=1:1

It should however be noted that these tests, dating from 1986, were performed on a gelatin-sized paper (Fabriano 5), which may have inhibited the platinum printout relative to palladium, see §11.5 that follows. However, more recent XRF measurements of a Pt:Pd = 1:1 sensitizer on a non-gelatin sized paper have yielded results somewhat better than those above: the Pt:Pd molar ratio was found to be ~ 1:2 in the middle tones, but only reached 1:1 in the maximum density exposures.⁷⁷⁵

It may be concluded from these results that, if an image containing approximately equal molar amounts of platinum and palladium is required, then the paper should be coated with a sensitizing solution in which the molar ratio of Pt:Pd = 2:1 or more. It should also be remembered that palladium is not as resistant to chemical attack as platinum, and may therefore be less permanent archivally, especially if chemical treatments are later applied to the print.

11.5 Effects of gelatin sizing on platinum printout

It has been emphasised at several points (§1.8, 5.2, 6.8, 7.6, 8.5) that in choosing a paper substrate, it is advisable to avoid those that are sized with gelatin, especially for the humid, print-out method of 100% platinum printing. It is on scientific record that proteins can bind strongly to platinum(II): the affinity of biological molecules such as collagen and DNA for platinum salts is reflected in the biological activity of chloro-complexes of platinum(II), which are highly allergenic, causing symptoms of asthma, dermatitis and urticaria, see §6.4.⁷⁷⁶

In 1989, the present author and research student, Neil Barnwell, confirmed by cyclic voltammetric studies that gelatin does indeed complex platinum(II) in aqueous solution and the resulting complex renders it less readily reducible to platinum metal by the iron(II) photoproduct.⁷⁷⁷ In spite of Willis's early warnings against it, some practitioners continue to recommend the use of gelatin sizing for platinum, because they find that it works with their particular *modus operandi*, which often involves a mixture with palladium, and they may be fortunate in their choice of gelatin, which at the present time is likely to be a highly-refined "food grade", unlike the crude "animal gelatins" of the 19th century used for paper sizing. In the last century, popular wisdom had it that: "Water is the Great Enemy of the Platinotype". It is important to understand why this is incorrect. Water enables the slow ligand substitution reaction of the platinum salt with gelatin, which is one of its true enemies:



Because ligand substitution reactions at Pt(II) are kinetically slow (§11.7), this reaction can take several hours to complete. If a freshly-coated develop-out platinum sensitizer is rapidly and totally dried, it will simply prevent this unfavourable reaction by minimising the time of contact with the hostile ingredient, gelatin, in the paper, thereby conserving the reactivity of the platinum(II) salt towards reduction by the iron(II) photoproduct upon development, in hot, concentrated potassium oxalate solution.

Platinum printing can therefore tolerate gelatin if the paper is rapidly dried immediately after coating, and kept dehydrated. Hence the 19th century strictures about desiccation referred to earlier. If the paper is pure, however, some humidity can be tolerated, so a gelatin-free paper is best for the printing-out platinotype (RH ca. 80%). Papers sized with alum-rosin or alkyl ketene dimer (Aquapel) are compatible with the process. It is a matter of historical record that Willis only succeeded with pure platinum printing by avoiding gelatin-sized papers (§5.2). It should be emphasised that this problem does *not* arise with palladium printing, which is much more reactive and not inhibited by gelatin. This may account in part for the swing towards palladium by many

contemporary, so-called 'platinum' printers. Certainly, the 100% platinum print is rarely made successfully today (§7.25). It is often the case in science that, to reach a 'simple' goal, one has to hack through through a jungle of complexities. The platinum–palladium medium demands a careful acknowledgement of all the chemical facts, and attention to detail. If the reader experiences any unaccountable failures in platinum printing on gelatin-sized papers, they may be explicable by considering the factors in the following summary:

- There are many types of gelatin, having differing aminoacid compositions: from bone, hoof, hide or skin; from rabbits, cows, pigs or seaweed; they may be treated in several ways – oxidised or not, deionised or not, acidified or not. It follows that some are likely to be stronger ligands and more inhibiting towards Pt(II) than others, especially those containing higher proportions of the thio–aminoacids, methionine and cysteine. They can greatly desensitize the chemical response by preventing the precipitation of platinum metal. Loss of highlight detail will be the first consequence, and almost total loss of image is an extreme possibility.
- The damaging reaction between gelatin and the usual platinum compound (tetrachloroplatinate(II)) is slow at room temperature – taking hours to complete. Heat makes it go faster. This reaction also requires the presence of water to bring the reagents into contact.
- **Temperature, Humidity, Concentration** and **Time** are therefore all crucial factors in determining the extent of the ill-effects caused by the gelatin. Obviously, high humidity (print-out) systems are most at risk; the bone-dry (development) systems least.
- In some circumstances (e.g. rapid drying, low humidity, pure gelatin at low concentration, short delays between coating and printing, cold workrooms) an acceptable platinum print may be obtained in the presence of gelatin. But it is unlikely to be as good as one made without.
- None of these problems arises with palladium, which prints easily and freely. So anyone using a mixture of platinum and palladium should satisfy themselves that there is actually a correct proportion of platinum in their resulting images, and that they are not just washing it down the drain and making palladium prints.
- The 'acid test' is the ability to make a premium quality 100% platinum print with your materials. You may be surprised how difficult it can be! (It took Willis 20 years to get it right.) Choice of a 'pure' paper is vital. I now use 'Buxton' paper, hand-made to my specification (see §8.7). Using the printing-out procedure described in §7.25, one can make a platinum print showing the same delicate highlight gradation as a palladium print – but it still requires care. There are now very few commercial papers that work well with 100% platinum, whereas most will work with palladium.

11.6 Characteristic curves by densitometry

Step tests made by the Malde–Ware print-out version, prepared as in §7, were densitometered using an X-Rite 312 densitometer in reflectance mode. As may be seen from the characteristic D/logH curves, in Fig. 11.3, of reflectance optical density versus log(relative exposure) the palladium sensitizer provides

the longest exposure scale ($\Delta\log H \sim 2.4$) and the lowest contrast in the mid-tones (slope $\gamma \sim 0.78$), compared with platinum (with the values $\Delta\log H \sim 1.9$ and $\gamma \sim 0.96$, respectively). The longer exposure scale of the palladium-containing sensitizers is seen to be due to a substantial non-linear 'toe' to the curve, which confers great tonal delicacy on the high values of a print. Mixtures of the two metals give intermediate values between these scales. The value of the maximum density, D_{\max} , for most of the tests was ~ 1.45 .

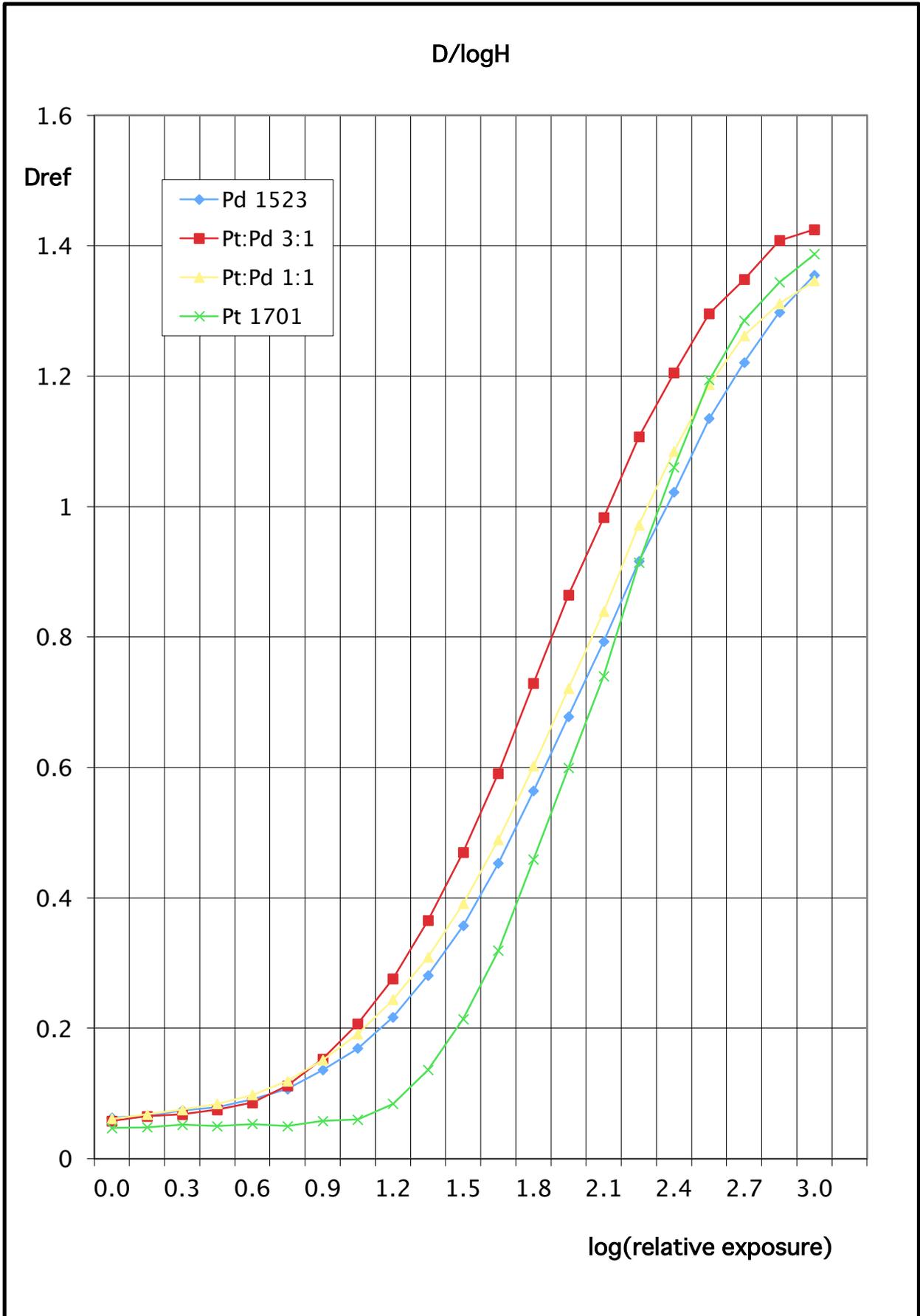
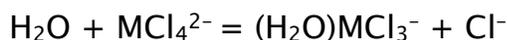


Fig. 11.3 D/logH curves for Pt, Pd, and Pt/Pd = 3:1 and 1:1 sensitizers

11.7 Aquation of platinum(II) and palladium(II)

The differences noted above between the characteristics of platinum and palladium printing papers may be summarised thus: palladium is faster to print and achieves a finer, smoother quality than platinum under a wider range of conditions and paper choices. This is due, in part, to the more labile solution chemistry of palladium(II) providing faster reduction reactions, but there is a more profound reason in that the state of aquation of the complex anion could be of critical importance in facilitating the path of the redox reaction. There is no easy route for imparting electrons onto the MCl_4^{2-} ion, but it may proceed more readily via the aqua-complexes $(\text{H}_2\text{O})\text{MCl}_3^-$ which are also present, and offer a more facile route to reduction by hydrogen atom transfer.⁷⁷⁸ For both metals in aqueous solution formation of an aquatrifluoro-anion occurs thus:



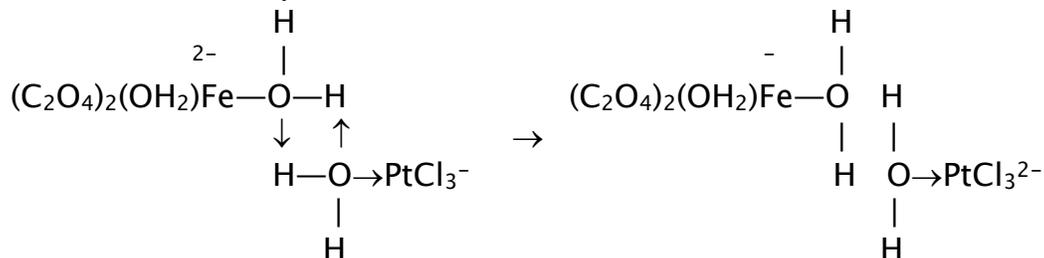
The equilibrium constant defined by:

$$K_{\text{aq}} = [(\text{H}_2\text{O})\text{MCl}_3^-][\text{Cl}^-]/[\text{MCl}_4^{2-}]$$

has the values at 20°C:⁷⁷⁹ $K_{\text{aq}} = 0.17$ for $\text{M} = \text{Pd}$, and $K_{\text{aq}} = 0.015$ for $\text{M} = \text{Pt}$, whence we may calculate that, at the typical concentration used for a sensitizer, >50% of the palladium is aquated, but <20% of the platinum is aquated which may account partially for the ease of reducing Pd(II). Moreover, establishment of the equilibrium is known to be very slow for platinum, a half-time of 2.4 hours has been measured for the reaction,⁷⁸⁰ so near-completion of the equilibrium nominally requires ten half-lives or ~24 hours. This explains why freshly-made solutions of tetrachloroplatinates(II) should be allowed to "mature" for 24 hours or so before first use (§6.3), and it may also account for the conflicting and uncertain figures quoted for the solubility of potassium tetrachloroplatinate(II).

11.8 The iron(II)-platinum(II) redox reaction

The pathway for the electron transfer from iron(II) to platinum(II) has not been elucidated, but in view of the labile nature of iron complexes with respect to ligand substitution it is unlikely to proceed via an 'inner sphere' mechanism, whereby the two coordination shells share a common bridging ligand. It is more probable that an 'outer sphere' mechanism operates, but this may still find a facile path via the partially aquated complexes:⁷⁸¹ if these are linked by a symmetrical hydrogen-bond bridge, then hydrogen atom transfer from octahedral $\text{Fe}(\text{C}_2\text{O}_4)_2(\text{OH}_2)_2^{2-}$ to square planar $(\text{H}_2\text{O})\text{PtCl}_3^-$, counterbalanced by proton transfer in the reverse direction, would result in a net electron transfer to form a transient Pt(I) species:

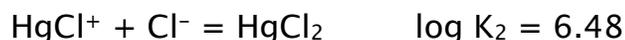
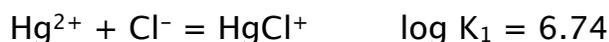


It is even possible that water molecules may mediate the process; a further electron transfer involving a second Fe(II) complex is required to complete the reduction, to give the overall stoichiometric result:

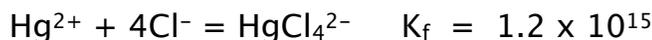


11.9 Effects of mercury(II), lead(II) and silver(I)

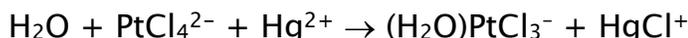
Since free chloride ions are liberated by the aquation reaction, the equilibrium in §11.7 will be moved to the right hand side by adding substances which bind with, and effectively remove free chloride ions from the system. Such 'scavengers' of Cl^- should increase the concentration of the Pt(II) aqua-complex, and thereby promote the ease of reduction to metallic Pt. The addition of mercury(II) salts, such as the nitrate, citrate or even the chloride, to the platinum sensitizer has long been recommended for sepia platinotype (§1.9, §6.7). It results in an image resembling that of palladium, *i.e.* having a lower contrast, brown colour and very smooth texture. The success of Hg(II) additives in improving the performance of platinotype formulae can be explained because Hg(II) binds Cl^- strongly in a covalent manner giving the molecule-ions HgCl^+ , HgCl_2 , HgCl_3^- , and HgCl_4^{2-} for which the equilibrium constants are:⁷⁸²



Overall:



The presence of mercury(II) will therefore promote the aquation reaction of the tetrachloroplatinate(II) thus:



and the higher concentration of the aquotrichloroplatinate(II) ion will enable easier reduction and better dispersion of the platinum within the cellulose fibres. HgCl_2 is also known to react with some Pt(II) complexes forming Pt-Hg bonds, so the chemistry may be more complex than is represented here.

Pb(II) salts may behave similarly as chloride scavengers, forming PbCl^+ , PbCl_2 , PbCl_3^- , and PbCl_4^{2-} . Lead is too electropositive for metallic Pb to be precipitated by the iron(II) photoproduct:

$$E^\circ(\text{Pb}^{2+}/\text{Pb}) = -0.126 \text{ V}$$

$$E^\circ(\text{PbCl}_2/\text{Pb}, 2\text{Cl}^-) = -0.266 \text{ V}$$

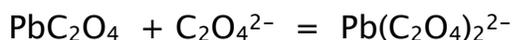
So it should remain in the Pb(II) state in the sensitizer and not contribute to the image substance. According to the extensive XRF measurements of Clarke the lead signal does not correlate with the image density, but is a more or less uniform background in the paper, suggesting that it is present as an insoluble colourless salt such as the oxalate or chloride. The aquation reaction above can also explain Willis's original preference for adding lead(II) nitrate to his sensitizers. In this case, the low solubility product of lead(II) chloride will scavenge chloride ions:

$$K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2 = 1.6 \times 10^{-5} \text{ at } 25^\circ\text{C}$$

but the possibility of forming a precipitate of PbCl_2 within the sensitizer seems rather undesirable. Some recipes (see §3.10 and §6.7) have recommended the use of lead oxalate, which is a very insoluble material:

$$K_{sp} = [\text{Pb}^{2+}][\text{C}_2\text{O}_4^{2-}] = 2.74 \times 10^{-11} \text{ at } 18^\circ\text{C}$$

but may acquire some solubility through complexation with free oxalate:⁷⁸³



The formation constant for the bisoxalato-plumbate(II) complex is 3.45×10^6 . For this equilibrium, it may be shown that the concentration is given by:

$$[\text{Pb}(\text{C}_2\text{O}_4)_2^{2-}] = 1.656 \times 10^{-3} [\text{C}_2\text{O}_4^{2-}]$$

Salts of both mercury(II) and lead(II) were much used by Willis as additives to his sensitizer formulations throughout the history of the Platinotype Company's papers, although lead was said by Willis's patents to be absent over the period 1880 to 1887, see §1.6 and §9.1. It is also significant that for the first five years of the platinotype process, 1873 to 1878 see §1.7, Willis also found it desirable to add silver nitrate to the sensitizer which, in addition to strengthening the image with silver metal, would also have acted to remove chloride ions, by forming insoluble silver chloride. This reaction has been used to prepare solutions of aquaplatinate(II) species:⁷⁸⁴



This hypothesis of scavenging the chloride ions is also supported by the experimental observation of the reverse effect: excess free chloride ions added to a Platinotype sensitizer (as alkali metal chlorides or hydrochloric acid) are found to inhibit the platinum image formation. Moreover, since chloride ions are released in the reduction of the platinum salt itself, according to reactions such as in §11.3 above, then there exists the possibility that the development of a platinum print may be chemically *self-inhibiting*, to an extent which depends on diffusion rates of chloride ion in the substrate, and the rate of adjustment of the equilibrium in §11.7. One result of this self-inhibition is that exposures for Platinotype are generally longer than those for Palladiotype, despite the fact that both use the same iron sensitizer, and palladium has the greater optical 'internal filter' effect (§12.3). More direct evidence for 'self-inhibition' has been observed by the author in the 'print-out' Platinotype process: the 'inhibition' of print values adjacent to heavy shadow regions, which may supply chloride ion by local diffusion during the printing exposure, as shown in §11.11.

To summarise the present hypothesis: scavengers of chloride ions promote the formation of the more easily reducible Pt(II) aqua-species, thereby accelerating the rate of reduction to Pt metal. Suggestions of any further experiments or data to test or falsify this hypothesis would be welcomed. A number of other metals that bind chloride well may also act thus: *e.g.* Zn(II), Cd(II), Cu(II), Tl(I), Sn(II), Bi(III). In 1885 a Professor Borlinetto claimed that addition of 10% of saturated copper chloride solution to a hot (176 °F) potassium oxalate developer produced a "warm sepia-brown tone", but this

option seems to have been little pursued.⁷⁸⁵ It may be significant that one sepia developer solution for platinotype recommended by Dr. Jacoby contained zinc oxalate,⁷⁸⁶ of which "the larger the quantity, the warmer the tone".

11.10 Mercury in platinotypes and palladiotypes

The effect of mercury(II) is not confined just to scavenging chloride ions, however. Because of its high redox potential with respect to the element:

$$E^{\circ}(\text{Hg}^{2+}/\text{Hg}) = +0.854 \text{ V}$$

mercury(II) is itself easily susceptible to reduction by the iron(II) photoproduct to give elemental metallic mercury which will co-precipitate with the platinum, although mercury is said not to form an amalgam directly with platinum. It is of some interest to determine the relative amount of mercury in finished images obtained by this means. Accordingly, a platinum sensitizer solution was prepared containing mercury(II) nitrate at a final concentration of 0.34 mol/dm^3 (molar ratio Pt:Hg = 1:1), coated and exposed for a range of times in the usual way. The amounts of mercury and platinum in the processed images were measured by quantitative X-ray fluorescence spectrometry, and compared with the amounts in the unexposed sensitized paper. Fig. 11.4 shows the variation with exposure time of the fractions of total metals deposited in the paper.

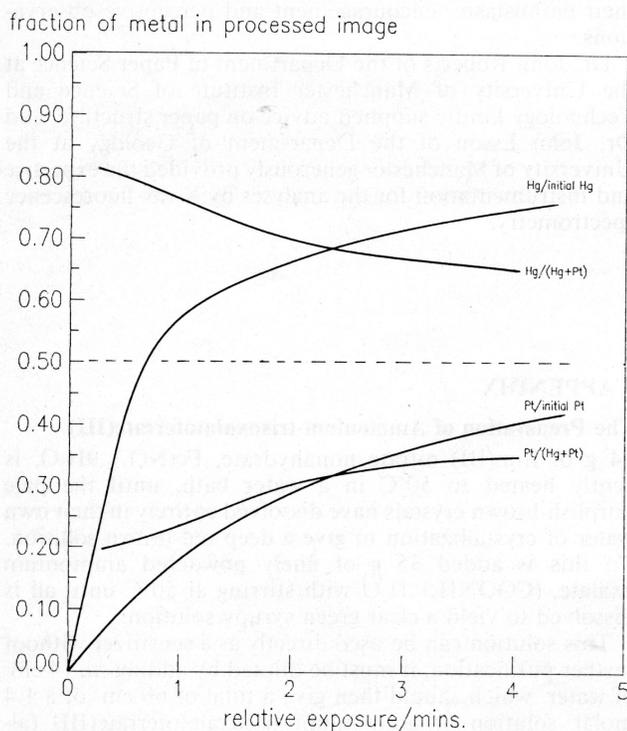


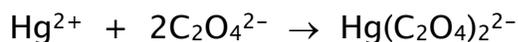
Fig. 11.4 Deposition of platinum and mercury from a Pt/Hg sensitizer

It can be seen that mercury is precipitated much more readily than platinum, consequently the proportion of mercury in the final image is always higher than in the sensitizing solution (1:1), the ratio Hg:Pt being ~4 at low exposures and ~2 at high exposures.⁷⁸⁷

Two different practices for adding mercury(II) salts to produce sepia tones were commonly employed historically (see §1.9): either by including the mercury(II) salt in the sensitizer – Willis's "S" papers – or by adding a mercury(II) salt, usually the chloride, to the oxalate developer solution, which was used hot. A third practice was to combine both these options together. In 2015 Lewis and Koseki investigated the quantitative consequences of these practices in samples of finished platinum prints, by analysis using XRF.⁷⁸⁸ Their findings show a clear difference for the two practices over a number of samples: at the concentrations normally employed, mercury-sensitized prints show a ratio Hg:Pt = 0.2–0.3, whereas mercury-developed prints have Hg:Pt = 0.8–1.1. The latter ratio range is also shown by prints made using both methods of including mercury(II).

The two options of adding mercury(II) – either to the sensitizer or to the developer – will certainly entail different chemistry. When mercury(II) salts are included in the platinum paper sensitizer, there is a further possibility of reaction between the mercuric chloride and the tetrachloroplatinate(II) anion, which may yield a molecule with a platinum–mercury bond. Such addition complexes are known and have been isolated and characterised for similar triphenylphosphineplatinum systems: Cl–Hg–Pt(PPh₃)₂Cl. Moreover, mercury(II) chloride has been shown to add to organocomplexes of platinum(II), to give Cl–Hg–PtMe₂Clbu₂bpy).⁷⁸⁹ The reduction of such heterobimetallic complexes to the metals might produce alloyed nanoparticles different from the form of Pt metal usually precipitated.

If, on the other hand, mercury(II) salts are added to the developer bath of concentrated potassium oxalate solution, as has been recommended by some early practitioners (§1.9), it can be predicted that they will be substantially converted to the stable bisoxalatomercurate(II) complex:⁷⁹⁰



for which the high formation constant diminishes the redox potentials:⁷⁹¹

$$E(\text{Hg}(\text{C}_2\text{O}_4)_2^{2-}/\text{Hg}, 2\text{C}_2\text{O}_4^{2-}) = +0.39 \text{ V}$$

$$E(\text{Hg}_2\text{C}_2\text{O}_4/\text{Hg}, \text{C}_2\text{O}_4^{2-}) = +0.41 \text{ V}$$

But the iron(II) potential (§11.3) is still low enough to reduce Hg(II) to elemental mercury. We note that Hg(I) is destabilised relatively by this complexation of Hg(II) because Hg(I), in the form of Hg₂²⁺ is not strongly complexed by oxalate for steric reasons, so its redox potential remains higher and its intermediate formation becomes less likely. It should also be noted that this system of Hg(II) and oxalate is photosensitive, so stored mercury(II)–containing oxalate developer may change with time;⁷⁹² historic instruction manuals say that the sepia developer is light-sensitive and "must be kept in the dark".⁷⁹³

The archival stability of historic platinum images containing mercury appears to be variable and unaccountable: some such images, possibly originally containing excessive amounts of mercury, have been observed to be faded (see §9.12). But there is also a growing body of evidence from XRF spectra (see §5.9) that many, if not all, of the sepia platinotypes made *circa* 1900, and now surviving apparently undegraded, do also contain mercury, as

expected from Willis's formulations (§1.9). To date, there has been no clear explanation put forward as to how the presence of mercury so strongly influences the colour of images in nanoparticle platinum, which does not form an amalgam, but the answer probably lies with Mie scattering theory, and a smaller particle size.

To seek an explanation for the variable and apparently inconsistent effects on image impermanence of mercury salts added either to the sensitizer or to the developer, one further chemical reaction of elemental mercury in the sensitized layer needs to be taken into account. It is an experimental fact that mercury vapour may be detected by its effect in blackening a paper impregnated with a tetrachloropalladate(II), and this has even provided a test for the presence of mercury.⁷⁹⁴ Evidently the elemental mercury is acting as a reducing agent towards the Pd(II), but the redox potentials

$$E^{\circ}(\text{Hg}^{2+}/\text{Hg}) = +0.854 \text{ V}$$

$$E^{\circ}(\text{Hg}_2^{2+}/2\text{Hg}) = +0.799 \text{ V}$$

$$E^{\circ}(2\text{Hg}^{2+}/\text{Hg}_2^{2+}) = +0.910 \text{ V}$$

$$E^{\circ}(2\text{Hg}^{2+}, 2\text{Cl}^-/\text{Hg}_2\text{Cl}_2) = +0.62 \text{ V}$$

are all too high, compared with the value for palladium:

$$E(\text{PdCl}_4^{2-}/\text{Pd}, 4\text{Cl}^-) = +0.62 \text{ V}$$

for a redox reaction to proceed, so the reaction must either involve the formation of the more accessible, insoluble mercury(I) chloride (aka calomel,⁷⁹⁵ Hg_2Cl_2):

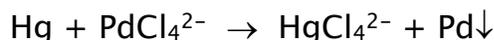
$$E^{\circ}(\text{Hg}_2\text{Cl}_2/2\text{Hg}, 2\text{Cl}^-) = +0.268 \text{ V}$$

or, if chloride ion is in excess, the chloro-complexed state of Hg(II):

$$E(\text{HgCl}_4^{2-}/\text{Hg}, 4\text{Cl}^-) = +0.38 \text{ V}$$

where the potential is diminished owing to the high formation constant for the tetrachloromercurate(II) complex ($K_f = 9 \times 10^{15}$). If oxalate ion is in excess, the oxalatomercurate complexes are also just accessible, as seen from the E values above, of ca. 0.4 V.

In these cases, metallic palladium can be precipitated by mercury vapour:



To see the noble metal mercury acting as a *reducing agent* in these circumstances is somewhat surprising and counter-intuitive. It appears that analogous reactions by mercury vapour can also reduce tetrachloroplatinate(II) to platinum metal, although this has not yet been tested by the author. The redox potential for platinum(II):

$$E(\text{PtCl}_4^{2-}/\text{Pt}, 4\text{Cl}^-) = +0.73 \text{ V}$$

is certainly high enough for the reduction to proceed:



but the kinetics of this reaction may be slow, and need to be measured. If the chemical product in sepia platinotype is indeed so variable – either elemental mercury or mercury(I) chloride or even tetrachloromercurate(II) – we may have a possible explanation for the inconsistent and variable observations on the stability of sepia platinotype images, depending on their method of preparation.

It will therefore be important in verifying this hypothesis to determine experimentally whether the mercury that is so commonly detected by XRF in sepia platinotypes is in the elemental state, and/or in the form a mercury(I) salt, as predicted above. If the latter substance is present, it should be possible to detect it by Raman spectroscopy in which the characteristic Hg–Hg stretching vibration falls at 167 cm^{-1} .⁷⁹⁶ It was suggested in §9.12 that elemental mercury can be completely lost from a kelainotype print due to its volatility. The formation of Hg_2Cl_2 or $\text{Hg}_2\text{C}_2\text{O}_4$ instead could account for the fact that mercury is not totally lost from sepia platinotype prints. The insolubility of Hg_2Cl_2 or $\text{Hg}_2\text{C}_2\text{O}_4$ would also prevent their being washed out of the paper during wet processing.

In contrast to the behaviour of platinum, we have found little change and no benefit in adding mercury(II) salts to any palladium sensitizer. Recent tests by Carver–Kubik indicate that the effect of mercury(II) is to “cool” the palladium image to a more neutral tone.⁷⁹⁷ Palladiotypes containing much mercury, such as those produced by Edward Weston, are therefore hard to understand, unless the practitioner himself added mercuric salts to his developer. Small amounts of mercury may simply be due to cross-contamination.

Unlike platinum, metallic palladium does form an amalgam with mercury, which would therefore greatly diminish the vapour pressure of the latter, and ensure its retention. It has recently been discovered that fully processed, dry palladiotype prints are capable of absorbing mercury vapour, probably from adjacent mercury-processed platinotypes, and that this mercury can be detected in the XRF spectra.⁷⁹⁸ Thus mercury can be transferred from some sepia platinotypes to palladiotypes, unless they are separated by an impermeable vapour barrier, such as polyester sleeves.

11.11 The 'inhibited edge' effect

It has been noted that in 100% platinum printouts made by the print-out method, there can be a deficiency of image along the border region between areas of very high density, and those of moderate density, as shown in fig. 11.5.

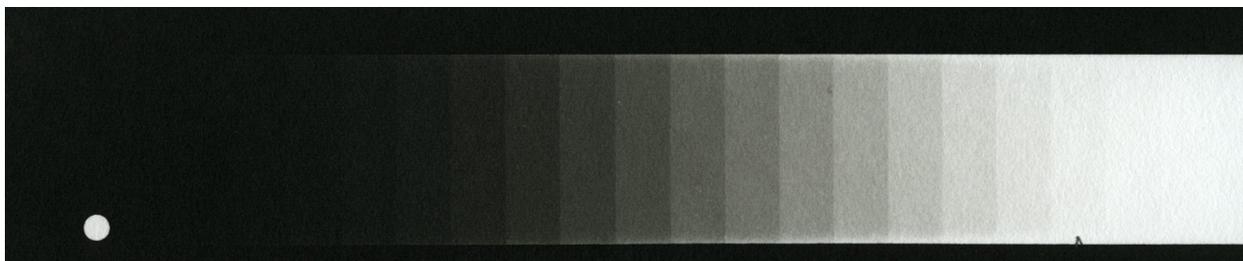


Fig. 11.5 100% platinum printout showing the "inhibited edge" effect.

This 'inhibited edge' effect is absent in palladium print-out, as shown in fig. 11.6.

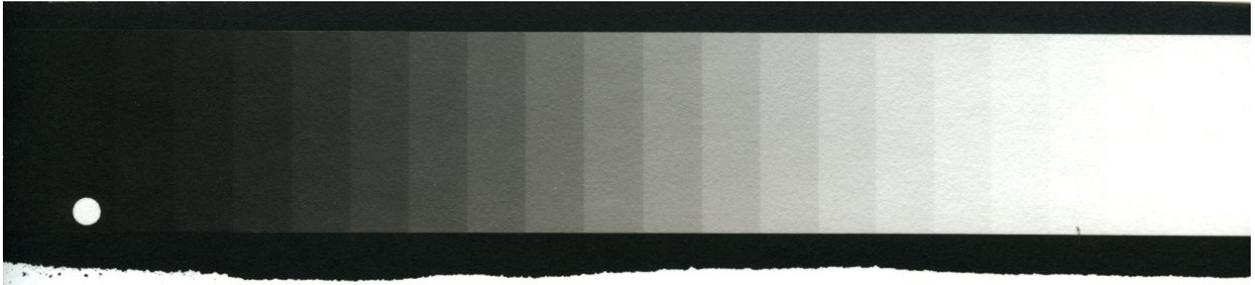


Fig. 11.6 100% palladium printout on Buxton paper.

It is also absent when the 100% platinum sensitizer is thoroughly dried, so there is much less print-out and little opportunity for diffusion, and the image is rapidly developed, fig. 11.7.



Fig. 11.7 100% platinum test, dried & developed.

If the potentially dense area in the test is masked with ruby lith, or physically cut off, before the exposure, then no image deficiency is observed. This suggests that the effect may be due to some reaction product diffusing out of the dense region, which locally inhibits the photochemistry in the moderate region. Of the species produced by the photochemical and redox reactions, it is most likely that chloride ion, Cl^- , is the cause of this inhibition, especially in view of the foregoing discussion in §11.7 and §11.9, although oxalate ions might also play a role in desensitising the Pt(II) complex to reduction.

An alternative, but less probable explanation is that the Pt(II) complex, experiencing a concentration gradient at the boundary, diffuses out of the lighter region during printout, so diminishing its availability for image formation.

This phenomenon may stem from the same cause as the contrary effect noted in §7.12 that the speed of platinum printout decreases with increasing RH, whereas the converse is true for palladium. It would therefore appear that the printout process is somewhat self-inhibiting with platinum, but not with palladium, for reasons examined in §11.7 and §11.9.

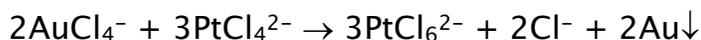
11.12 Effects of gold(III)

It has been recommended that salts of gold(III) such as the chloride (actually tetrachloroauric acid, $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) may be added to a platinum sensitizer to 'tone' the image and improve its quality. But, in view of the redox potentials:

$$E^\circ(\text{AuCl}_4^-/\text{Au}, 4\text{Cl}^-) = +1.00 \text{ V}$$

$$E^\circ(\text{PtCl}_6^{2-}/\text{PtCl}_4^{2-}, 2\text{Cl}^-) = +0.68 \text{ V}$$

it is evident that tetrachloroauric acid should oxidise the platinum(II) in the sensitizer to platinum(IV) and be itself reduced to metallic gold:

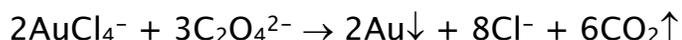


An investigation of the reaction between platinum(II) and gold(III) has shown it to be rapid at low concentrations,⁷⁹⁹ with the formation of an intermediate gold(I) complex, presumably AuCl_2^- ; but the latter is not stable at higher concentrations and will disproportionate to gold(III) and gold metal.⁸⁰⁰ Tests on the platinum sensitizer solution, to which tetrachloroauric acid or ammonium tetrachloroaurate was added, showed the precipitation of metallic gold to be quite rapid; *i.e.* any more than a trace of gold(III) in a platinum sensitizer will be decomposed before it can even be coated or exposed, and will simply impart a fog of nanoparticle gold to the paper, which is often coloured lilac or purple. There seems little to be gained from its use.

This not true of palladium, however, due to its higher redox potential:

$$E^\circ(\text{PdCl}_6^{2-}/\text{PdCl}_4^{2-}, 2\text{Cl}^-) = +1.288 \text{ V}$$

a mixed gold(III)/palladium(II) solution is stable with respect to oxidation–reduction, and may be used as a sensitizer. Even so, precautions must be taken with this sensitizer, because gold(III) will quite rapidly oxidise any free oxalate ions arising from the partial dissociation of trisoxalatoferate(III) – see §10.5:



Provided that the ambient temperature is not too high and that the coating and drying operations are carried out rapidly, it is possible to make good quality mixed images in gold–palladium. These can display quite a wide range of colours, depending on the exact chemistry.

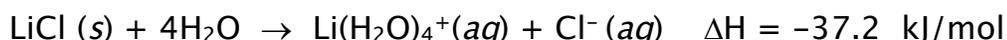
11.13 Choice of cation

As has previously been indicated, the print–out process is dependent on the presence of sufficient water in the paper fibres, and this can be controlled by several factors: the choice of cation, the ambient RH, or the addition of humectants. A hygroscopic cation, which attracts water molecules to itself, binding them in a primary hydration sphere, will not immediately benefit the image print–out process, because none of the water so absorbed is available initially as a solvent for the iron(II) and noble metal anions. One of the worst cations in this respect is lithium, Li^+ . Although lithium salts are extremely hygroscopic and often deliquescent, they have to take up and bind a large quantity of water in the secondary hydration sphere, before sufficient can be usefully liberated to mobilise the *other* ions, which have less affinity for water.

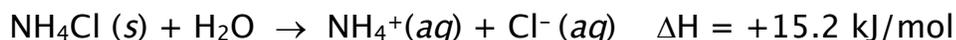
The resulting sensitizer layer has to be brought to a state of wetness which is uncontrolled and liable to damage negatives in contact, unless a thin plastic film is interposed between them. This inconvenience, of course, can degrade the image sharpness.

The cations of lithium, and sodium to a lesser degree, are known in aqueous solution chemistry as *structure-making* cations, because they bind water molecules strongly, whereas what is really needed here to promote aqueous diffusion is the converse: a *structure-breaking* cation. This property can be provided by the ammonium cation, which is similar in its molecular structure to water, and assists the absorption of water in a disordered state without binding it strongly. In consequence, if ammonium is employed as the sole cation, only a relatively small amount of water need be absorbed to provide sufficient ion mobility to enable a print-out process.

The difference in the thermodynamics of hydration between lithium and ammonium cations can be readily experienced in practice: when lithium chloride is dissolved in water, the solution becomes hot. The dissolution reaction is exothermic, driven by the spontaneous evolution of heat energy (enthalpy ΔH) due to the making of bonds between lithium ions and water molecules.



In contrast, when ammonium chloride is dissolved in water the solution becomes cold; here the endothermic reaction proceeds spontaneously, in spite of the need to absorb heat from the surroundings, because it also entails a large positive entropy change (ΔS), due to the structure-breaking effect causing an increase in the disorder of the system.



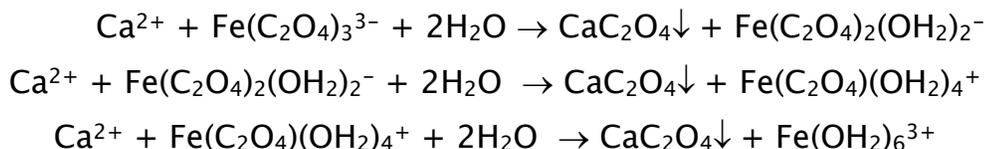
Deeper discussion of these factors requires some acquaintance with the concepts of the Second Law of Thermodynamics, such as entropy, ΔS , and the Gibbs Free Energy, ΔG , which determines if a reaction will be spontaneous.

The inappropriateness of lithium as a cation for these processes becomes obvious if it is used in a pure platinotype sensitizer, where it will totally inhibit the print-out process. Sodium as cation also works very poorly for print-out platinotype. Only with the more energetic and facile metal redox processes – palladium and gold – can these cations be used successfully, but high degrees of hydration may be called for, with increased risk to the negative. Moreover, using these cations at low RH can cause the image quality to deteriorate, and give rise to solarization on development – a reversal of the tonal scale in regions of heavy exposure.

It should be noted that the larger alkali metal cations, potassium, rubidium and caesium, while less hygroscopic than lithium or sodium, are also unsuited to the iron-based processes, but for a different reason: they tend to form salts of low solubility with either the ferrioxalate anion or the complex tetrachlorometallates of platinum, palladium, and gold. Low solubilities mean low sensitizer coating weights and consequently weak images, unless double coating is employed, which often proves counter-productive. If one resorts to

the inconvenience of hot, or supersaturated solutions, in an attempt to overcome this disadvantage, then crystallization is likely to prove a problem.

Nor is calcium a good choice for the cation, because of the insolubility of calcium oxalate (it is the principal constituent of gall- and kidney-stones!), which is comparable with that of calcium carbonate. Its formation in the sensitizer will tend to promote the aquation and hydrolysis of the ferrioxalate anion, with the eventual generation of iron stains of ferric oxyhydroxide.



To sum up: there are very good physico-chemical reasons why ammonium should be the cation of choice in the print-out iron-based processes, if the quality of the image and the ease of working are held to be important.

11.14 Optical properties of metal nanoparticles

The noble metal precipitated by these photochemical means usually has a particle size in the nanometer region, 15–25 nm, as demonstrated by the electron microscopy of Patrick Ravines, §5.10 and Matthew Clarke, §5.7. These nanoparticles have "colloidal" dimensions,⁹ in contrast to the much larger micron-sized bundles of filamentary metallic silver formed in most developed silver-gelatin photographic materials. The chemistry and physics of metallic nanoparticles are attracting great interest at the present time,⁸⁰¹ although the recognition that metals in the finely divided state can cause distinctive colours goes back to Michael Faraday in 1857.⁸⁰² With sizes less than the wavelengths of visible light, metal nanoparticles display interesting optical characteristics due to the excitation by light of collective oscillations in their conduction electrons, which are known in quantum-mechanical language as *plasmons*. For most metals, such *surface plasma resonance* generally gives rise to absorption maxima in the ultra-violet region of the spectrum, but in a few cases, notably copper, silver and gold, the variation of the dielectric function of the metal with frequency causes quite sharp absorption bands in the visible region, giving rise to the striking colours that first attracted Faraday's attention.

A theoretical treatment of this phenomenon for spherical metal particles was worked out by Gustav Mie in 1908,⁸⁰³ using Maxwell's electromagnetic theory, and was subsequently extended to ellipsoidal particles by Gans.⁸⁰⁴ When the particles are much smaller than the wavelength of light a dipolar approximation is valid and absorption predominates but, at larger radii, multipolar terms become important and light scattering also becomes significant. This topic has been taken up again and greatly extended by Milton Kerker.⁸⁰⁵ Recently, Creighton and Eadon have calculated absorption spectra for

⁹ *Etymological footnote 9: the word 'nanoparticle' is now preferred to the older usage 'colloidal' to describe finely-divided metals. The word "colloid" now tends to be reserved only for "gummy" macromolecular substances. (Greek: kolla = χολλα = glue).*

10 nm diameter particles of most of the metallic elements; their work shows that distinctive colour is a relatively uncommon property among nanoparticle metals: the surface plasmon absorption band only peaks in the visible region for the alkali metals, alkaline earths, coinage metals, and scandium, yttrium, europium and ytterbium. In view of the requirement for a useful pigment to be chemically inert, it follows that copper, silver and gold are likely to remain the only metals in the nanoparticle state providing distinctive colours for decorative or image-making purposes, other inert metals being grey or brown in this state.⁸⁰⁶ A brown colour, often seen in palladium images, implies that there is a stronger absorption of blue light than the rest of the visible spectrum, conferring the complementary colour, red; it arises characteristically when the nanoparticles are smaller – the result of more rapid reaction kinetics, due to elevated temperatures or more vigorous developing agents. Restricted humidity can also inhibit particle growth, and ‘brown’ the image, as seen in §11.15.

The colours of nanoparticle metals may be modified by several factors besides the particle size and departure from sphericity mentioned above. For instance, the linear aggregation of spherical particles causes the appearance of a long wavelength absorption band due to the splitting of the degenerate surface dipolar plasma mode into lateral and longitudinal components, similar to a prolate spheroid. The plasmon absorption band is also shifted by the presence of molecules or ions adsorbed onto the surface of the particle, where the metal atoms are coordinatively unsaturated.⁸⁰⁷ Henglein has also shown that nanoparticle silver can act as an electron pool towards redox active species, and that the stored charge influences the plasma resonance absorption.⁸⁰⁸ These factors are responsible for some striking changes in the colours of nanoparticle metal images during their wet-processing procedures. As Sriharsha Karumuri explains, in his downloadable Powerpoint presentation on Mie theory:

"The surface plasmon resonance peak changes with its own dielectric properties and those of its local environment including the substrate, solvent, and adsorbates. This principle that the high sensitivity of the surface plasmon resonance spectrum of noble metal nanoparticles to adsorbate-induced changes in the dielectric constant of the surrounding nanoenvironment is used in chemosensing and biosensing."⁸⁰⁹

Recent developments in the theory of nanoparticle optical spectra include measurement of the size dependence of the plasmon absorption,⁸¹⁰ and methods for solving Maxwell's equations for light scattering from particles of arbitrary shape in a complex environment,⁸¹¹

11.15 Factors influencing image colour

The theory of light-scattering by metal particles due to Gustav Mie, and extended by others as summarised above, shows that the following physico-chemical properties are important in determining the colour of a Pt/Pd image composed of metal nanoparticles:

- Chemical composition of image substance(s) – proportions of Pt and Pd.
- Particle size distribution and particle shape.
- Presence of adsorbates affecting surface plasmon resonance spectrum.
- Refractive index of the host matrix supporting the image nanoparticles.

The quantity of water present in the sensitized cellulose fibres will have an important governing effect on the resulting size of the nanoparticle image substance, and hence on the colour of the image, especially for the print-out, rather than the development process. A large 'reservoir' of fibre water will permit greater amounts of substances to react locally during exposure and therefore make it possible for the particles of metal to grow larger. Such particles will appear more neutral in hue. A very restricted 'pool' of fibre water will constrain the chemistry to producing small metal particles only, which can show quite marked colours – brown or sepia for silver and palladium, rather than black; and even pink, magenta and blue in the case of gold. Thus, regulating the hydration of the paper before exposure controls the colour of the printed-out image. Cellulose itself absorbs water to a degree that is well-documented, as indicated above, but the concentration of water in the paper fibres will also depend on the other chemicals present in the sensitizer, especially on the cations used for the complex salts of iron and the noble metal.

Pure platinum images obtained by the modern print-out method have a neutral grey tone that only becomes slightly warmer at low values of relative humidity (<55% RH). In contrast, the palladium sensitizer displays a marked change in image colour with relative humidity, passing from a red-brown at 32% RH (essentially still a development process in which the high values may be quite dichromatic), through a pleasing purplish-brown at 55% RH to a neutral grey-black at 80% and above – see Fig 11.8. Mixtures of the two metals produce corresponding intermediate results, which allow the printer some scope in choosing the image colours – see Fig. 11.7. In platinum-palladium practice it is found that many factors need to be controlled in order to obtain reproducible colour. The presence of any of the following substances in the sensitizer tends to promote a brown coloration in platinum-palladium prints:

- 1. Proportion of palladium in the sensitizer**
Palladium tends to give warm brown images whereas platinum tends to yield neutral grey tones. The proportions of Pt and Pd in the image will not be the same as in the mixed sensitizer: generally Pt is precipitated more slowly than Pd, because the former can be inhibited by many substances, so the latter tends to predominate.
- 2. Concentration of surfactants in the sensitizer**
Surfactants, *e.g.* Tween 20, may tend to stabilize smaller nanoparticles by surface adsorption, inhibiting particle growth and therefore causing warmer colour. To make neutral-toned palladium prints the Tween concentration should be no more than 0.1% or preferably totally absent.
- 3. Presence of other reactive metal salts**
e.g. Hg(II), Pb(II), Cd(II), Cu(II) and Zn(II) in the sensitizer or developer may affect the rate of reduction of Pt, be co-precipitated, or surface adsorbed. Hg(II) salts particularly induce a strong sepia colour in Pt prints.
- 4. Presence of gelatin sizing agent in the paper**
This may interact, like the surfactants, by 'protecting' nanoparticle metals, favouring formation of smaller particles and therefore warmer colours.

Gelatin also seriously inhibits the precipitation of platinum. Sizing by starch, alum–rosin, or alkyl ketene dimer (AKD or 'Aquapel') gives more neutral tones with palladium.

5. **Residual iron(III) in the paper**

This is due to imperfect clearing of the print, and can cause the slow appearance (over months or even years) of a yellow stain in the highlights, and a warming of the image colour. Its presence may be promoted by alkaline–buffered papers, containing chalk.

6. **Temperature of the development bath**

'Hot bath' development of platinotypes may very slightly warm the tones at temperatures of 60–70°C. This is less significant for print–out where the metal nanoparticles are already formed during the exposure.

The following listed parameters tend to promote more neutral grey colour in palladium prints as they are *increased*, and conversely tend to promote a brown colour as they *decrease*, so all must be considered if neutral grey tones are desired from a palladium sensitizer, which can be quite difficult to achieve. It *is* possible to make neutral coloured prints of pure palladium if attention is paid to all the factors.

7. **Concentration of humectants in the sensitizer**

Their presence may promote an increased amount of water to be absorbed by the cellulose fibres. Possible humectants like glycerol, ammonium nitrate, and dimethylsulphoxide are hygroscopic. Cations such as Li⁺ and Na⁺ are strongly hydrated and deliquescent and promote humidity; NH₄⁺ is the most favourable cation for humidification, for thermodynamic reasons.

8. **RH of ambient atmosphere: pre–humidification**

Higher RH in the atmosphere increases the amount of absorbed water in the sensitized sheet, which enables mobility of the ions for print–out, and growth of metal nanoparticle size, giving more neutral colour. RH control before exposure is important in print–out Pt/Pd, and can be achieved by constant humidity enclosures, containing saturated salt solutions, or even water for a timed humidification. See Fig. 11.8, §11.16.

9. **Temperature of the ambient atmosphere**

For a given RH, a higher temperature determines a higher water content of the atmosphere, *i.e.* the *absolute* humidity is greater, so it promotes more neutral tones. *e.g.* 56% RH @ 25°C is the same absolute humidity as 75% RH @ 20°C. For a conversion table for absolute humidities see Table 11.1.

10. **Paper base composition**

The differing fibre morphology of celluloses derived from flax (linen) versus those from cotton may favour different sized metal nanoparticles. Palladium prints are more neutral–toned on linen than on cotton paper.

11. **Duration of storage time (non–desiccated)**

between coating the paper and exposing it – if the RH is high there may be

slow (~days) reaction of Pt(II) salt with e.g. gelatin, oxalate ions, etc. Most practitioners favour coating and printing the same day.

12. **Atmospheric pressure during exposure**

i.e. whether using a pressure frame or a vacuum easel for the contact exposure: vacuum pumping can reduce the amount of absorbed water and tends to produce warmer toned prints with Pd. Carbon dioxide is always evolved during the exposure, so will seek a pathway to escape from the paper: porous felt backing is recommended for the contact printing frame.

13. **Exposure duration**

Metal nanoparticle growth during print-out depends on the range of diffusion of the reactants, and is therefore time-dependent. Lengthy exposures of palladium papers at lower light intensity are more likely to give neutral-tones than brief exposures at higher intensity.

14. **Higher temperature during exposure**

increases diffusion rates of ions to build metal particles, so should promote neutral colour of print-out (but this has not yet been tested).

15. **Post-humidification by "steaming"**

over warm water (typically @ 40°C for 2 minutes) – after exposure but before wet development – may tend to shift the colour of palladium prints towards more neutral tones. It also consolidates the print-out image before wet processing, diminishing any development.

16. **Chemistry of developer**

In development processing, the chemistry of the first clearing bath affects the colour of palladium prints, which are warmer with oxalate than with citrate, see Fig. 6.7, §6.18. The Platinotype Co. formulated a phosphate-containing developer said to provide colder tones with platinum.

17. **Toning**

involving the deliberate deposition of new substances onto the image. *e.g.* Packham's catechu 'warms' Pt images; Dollond's gold toning 'cools' them.

18. **Waxing, varnishing, or burnishing**

of the paper surface in order to fill the interstices between the cellulose fibres may affect the refractive index of the host medium and change light scattering by the image. The wax or varnish may itself be coloured, or the source of future deterioration.

19. **Spectral emissivity of the printing light source**

No direct effect of this has been evident, but any heating (IR content) may reduce the amount of absorbed water, favouring warmer tones; *e.g.* HID lamps or sunlight versus UVA fluorescent tubes.

20. **Negative substrate**

No difference in effect has yet been noted between using digital negatives printed on ceramic-coated plastic film (*e.g.* Pictorico) compared with silver-gelatin negatives.

11.16 Control of humidity

The influence on image colour of the RH of the sensitizer before exposure can be seen in these tests (Fig. 11.8) of a 1:1 Pt:Pd printout, using the same sensitizer solution on 160 gsm Buxton paper at RH values of 80%, 56% and 15%. The absolute humidities of atmospheres, in milligrams of water per cubic decimeter (litre), as the RH varies with temperature are given in Table 11.4. Substances suitable for maintaining a range of constant humidity atmospheres by means of their saturated solutions are listed in Table 11.5, with their essential properties.⁸¹² The construction and use of constant humidity boxes is described in §7.18.

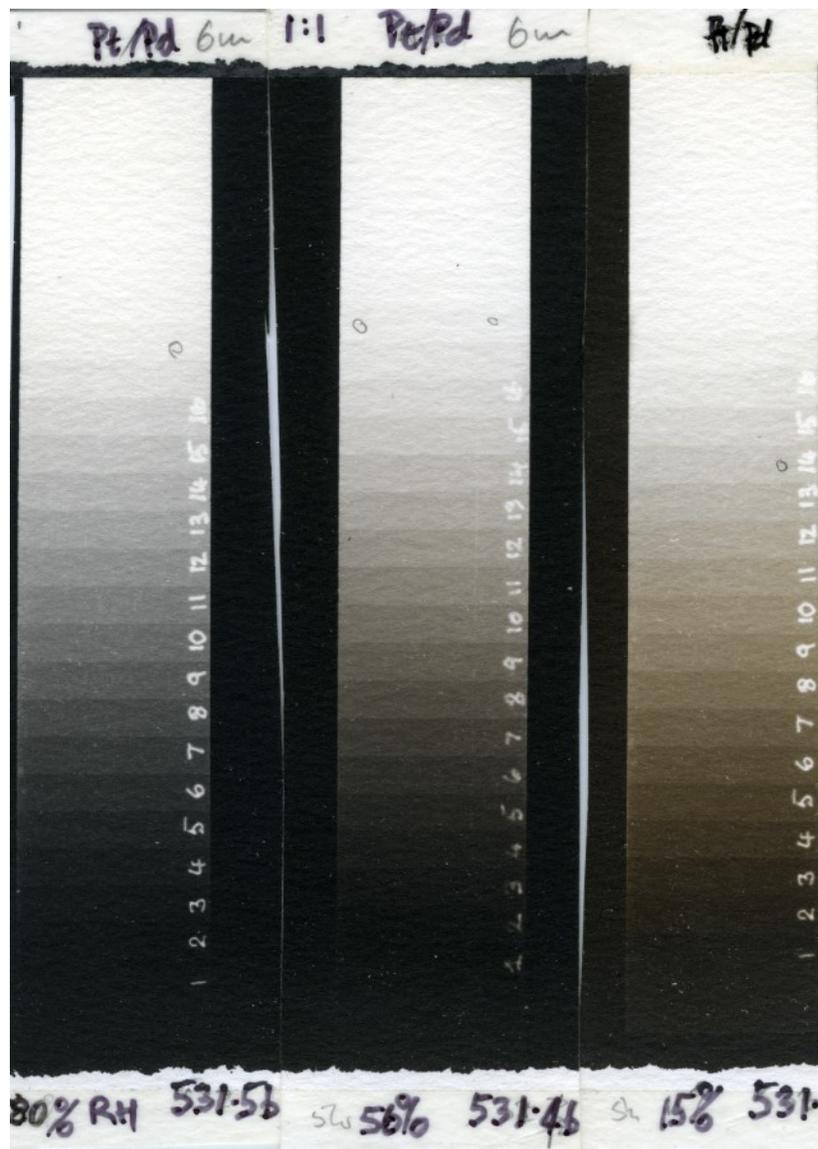


Fig. 11.8 The effect of RH on colour of Pt/Pd printout⁸¹³

%RH 20°C	100	95	90	85	80	75	70	65	60	55	50	45	40	35	30	25	20	15	10	5	
H ₂ O mg/l	17.30	16.44	15.57	14.71	13.84	12.98	12.11	11.25	10.38	9.52	8.65	7.79	6.92	6.06	5.19	4.33	3.46	2.60	1.73	0.87	
T°C																					
10	9.40										92	83	74	64	55	46	37	28	18	9	
11	10.01									95	86	78	69	60	52	43	35	26	17	9	
12	10.66								97	89	81	73	65	57	49	41	32	24	16	8	
13	11.35							99	91	84	76	69	61	53	46	38	30	23	15	8	
14	12.07						100	93	86	79	72	64	57	50	43	36	29	21	14	7	
15	12.83						94	88	81	74	67	61	54	47	40	34	27	20	13	7	
16	13.63					95	89	83	76	70	63	57	51	44	38	32	25	19	13	6	
17	14.84			99	93	87	82	76	70	64	58	52	47	41	35	29	23	17	12	6	
18	15.37			96	90	84	79	73	68	62	56	51	45	39	34	28	23	17	11	6	
19	16.21		96	91	85	80	75	69	64	59	53	48	43	37	32	27	21	16	11	5	
20	17.30	100	95	90	85	80	75	70	65	60	55	50	45	40	35	30	25	20	15	10	5
21	18.34	94	90	85	80	75	71	66	61	57	52	47	42	38	33	28	24	19	14	9	5
22	19.43	89	85	80	76	71	67	62	58	53	49	45	40	36	31	27	22	18	13	9	4
23	20.58	84	80	76	71	67	63	59	55	50	46	42	38	34	29	25	21	17	13	8	4
24	21.78	79	75	71	68	64	60	56	52	48	44	40	36	32	28	24	20	16	12	8	4
25	23.05	75	71	68	64	60	56	53	49	45	41	38	34	30	26	23	19	15	11	8	4
26	24.38	71	67	64	60	57	53	50	46	43	39	35	32	28	25	21	18	14	11	7	4
27	25.78	67	64	60	57	54	50	47	44	40	37	34	30	27	23	20	17	13	10	7	3
28	27.24	64	60	57	54	51	48	44	41	38	35	32	29	25	22	19	16	13	10	6	3
29	28.78	60	57	54	51	48	45	42	39	36	33	30	27	24	21	18	15	12	9	6	3
30	30.38	57	54	51	48	46	43	40	37	34	31	28	26	23	20	17	14	11	9	6	3
31	32.07	54	51	49	46	43	40	38	35	32	30	27	24	22	19	16	13	11	8	5	3
32	33.83	51	49	46	43	41	38	36	33	31	28	26	23	20	18	15	13	10	8	5	3
33	35.68	48	46	44	41	39	36	34	32	29	27	24	22	19	17	15	12	10	7	5	2
34	37.61	46	44	41	39	37	34	32	30	28	25	23	21	18	16	14	11	9	7	5	2
35	39.63	44	41	39	37	35	33	31	28	26	24	22	20	17	15	13	11	9	7	4	2
36	41.75	41	39	37	35	33	31	29	27	25	23	21	19	17	15	12	10	8	6	4	2

Table 11.4 RH % Values at various temperatures equivalent to those at 20°C (in absolute water content [H₂O] mg/litre)

Substance	Formula	RH% (20°C)	Solubility (g/l)
Calcium chloride	CaCl ₂	~9	solid
Lithium chloride	LiCl	15	800
Potassium acetate	CH ₃ COOK	20	2560
Calcium chloride	CaCl ₂	32	750
Potassium carbonate	K ₂ CO ₃ .2H ₂ O	44	1100
Calcium nitrate	Ca(NO ₃) ₂ .4H ₂ O	56	1290
Magnesium acetate	Mg(CH ₃ CO ₂) ₂ .4H ₂ O	65	1200
Sodium chloride	NaCl	76	360
Ammonium chloride	NH ₄ Cl	80	372
Potassium chloride	KCl	86	340
Sodium carbonate	Na ₂ CO ₃ .10H ₂ O	92	215
Potassium nitrate	KNO ₃	95	316

Table 11.5 Substances for making constant RH enclosures.

The chemicals listed in Table 11.5 above have been selected for their convenience, relative cheapness, and low toxicity. For practical purposes, and in the interests of economy, you can start with only three controlled humidity chambers containing, respectively, solid anhydrous calcium chloride (RH 9%), saturated calcium chloride (RH 32%) – which is conveniently made from the solid when it becomes too tacky – and either ammonium chloride (RH 80%) or common salt (RH 75%). The RH in such a system varies very little with temperature provided a saturated solution is maintained (The natural tendency for the vapour pressure of water to increase with temperature tends to be offset by an increase in the solubility of the salt, in most cases). However the absolute humidity, measured as the weight of water per unit volume of air, does increase with temperature as shown in Table 11.4.

An alternative, less precise, method of humidity control is kinetic in nature and requires a timed exposure of the dried paper to a 100% RH environment, *i.e.* over pure water. The result for a palladium sensitizer on Fabriano 5 paper is shown in Fig. 11.9. The sensitized paper was initially dried to RH ~10%, and the time intervals of exposure of successive strips were 5, 10, 20, 40 and 80 minutes.

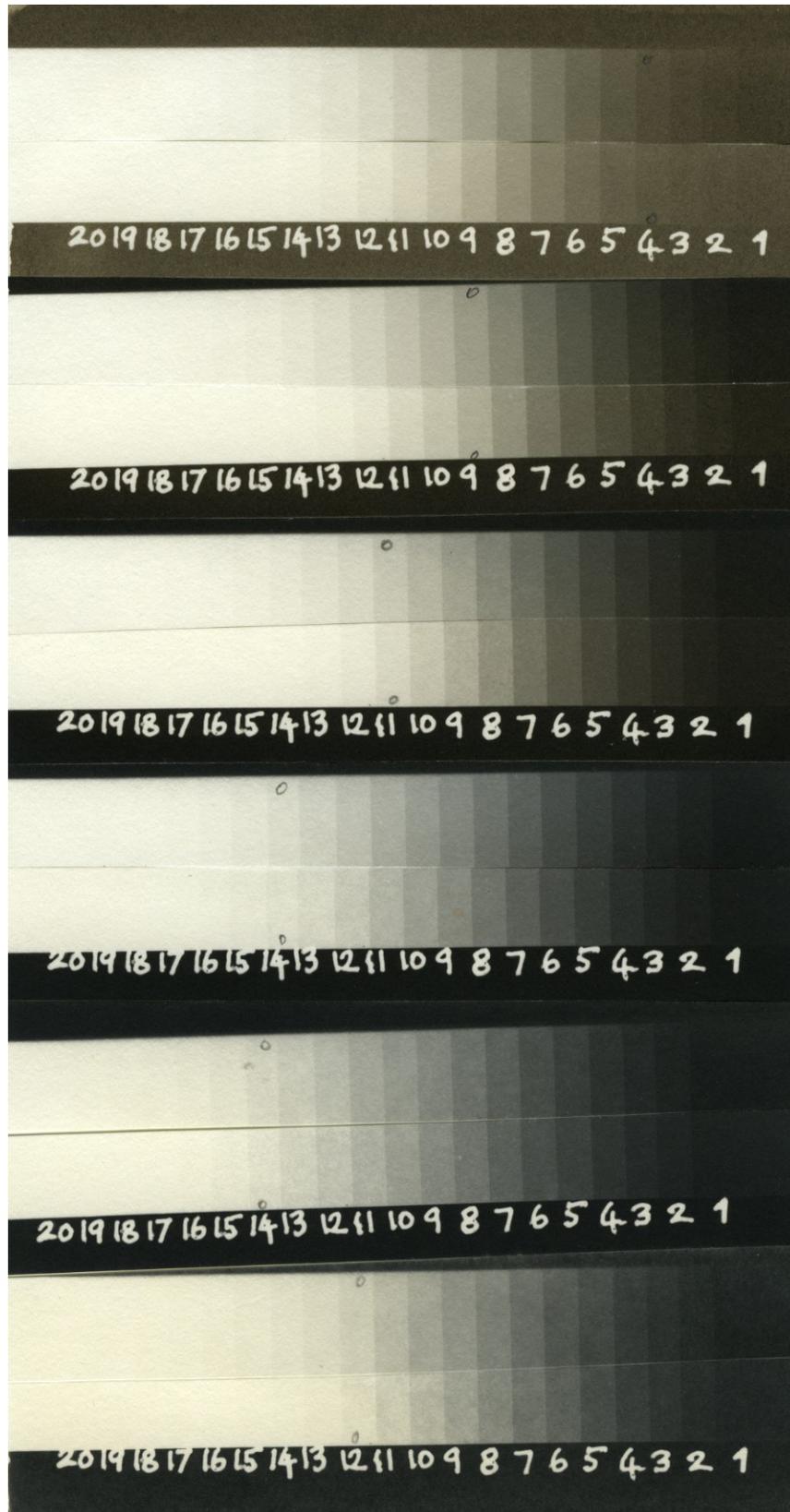


Figure 11.9 Effect on palladium of timed exposure to 100% RH

12. Quantitative Aspects of Siderotype Photochemistry

There are four main factors influencing the photochemical yield of an alternative photographic printing process and the way it depends on the wavelength of the radiation used to make the print:

- (1) Spectral emissivity of the light source
- (2) Photochemical quantum efficiency – variation with wavelength
- (3) Fraction of incident light absorbed by the photoactive species
- (4) Absorption of actinic light by printing equipment, e.g. glass platen

Each of these will be discussed in turn below, and then all four combined to calculate the wavelength dependence of the yield of image substance, and the duration of exposures that can be expected for typical UV light sources.

12.1 Spectral emissivity of light sources

The spectrum of energy emitted by a light source varies with the wavelength in a manner shown, for example, in Fig. 12.1 for a Philips lamp of type actinic/05.

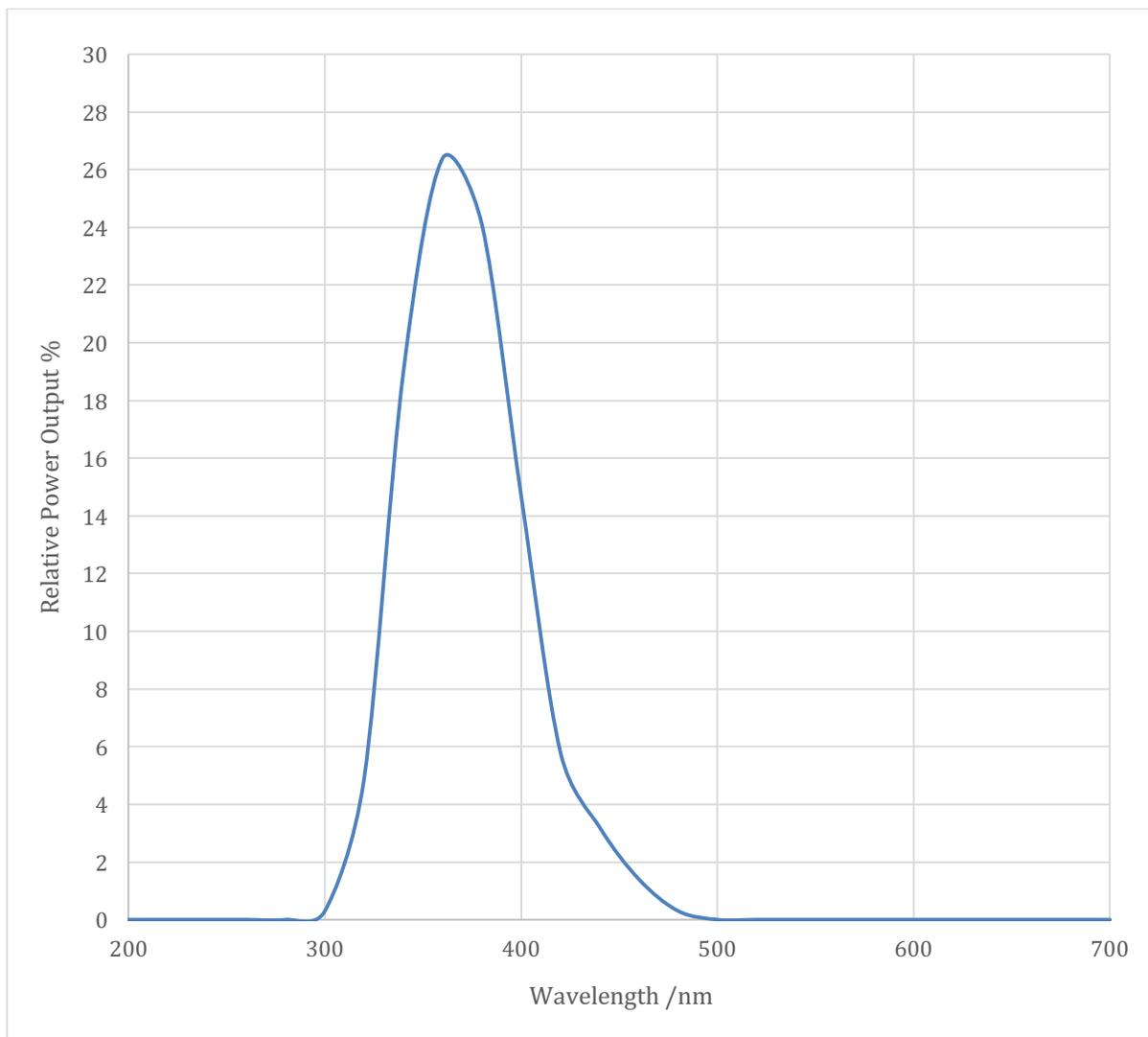


Fig. 12.1 Relative output of Phillips Actinic/05 UV lamp

This is typical of a commercial UVA mercury source. It is the area under this curve, between appropriate wavelength limits, that determines the yield, not just the height of the peaks in the emissivity. The spectral power per unit bandwidth must be integrated over the wavelength range. In practice this can be done by taking thin slices of the spectrum every 10 or 20 nm, calculating the effect at each sample wavelength, and summing the results over the whole wavelength range. More simply, the approximate proportions of lamp output at various wavelengths are tabulated in Table 12.1:

Wavelength	300	320	340	360	380	400	420	440	460	480	nm
Rel. Output	0.3	4.9	19.0	26.4	24.1	14.7	5.8	3.2	1.4	0.3	%

Table 12.1 Relative output of Philips type actinic/05 UV lamp.

12.2 Wavelength dependence of quantum yield

The intrinsic response of the primary photochemical process is expressed by the quantum efficiency, or quantum yield, ϕ . For the photolysis of the trisoxalato ferrate(III) ion in aqueous solution this has been determined reliably at several wavelengths of the mercury emission spectrum by a number of independent workers.⁸¹⁴ All agree that a value of ϕ slightly greater than unity obtains over the wavelength range from 250 to 450 nm, but begins to fall off sharply above 500 nm, becoming insignificant in the green/yellow regions of the spectrum and beyond, as shown in Fig. 12.2.⁸¹⁵

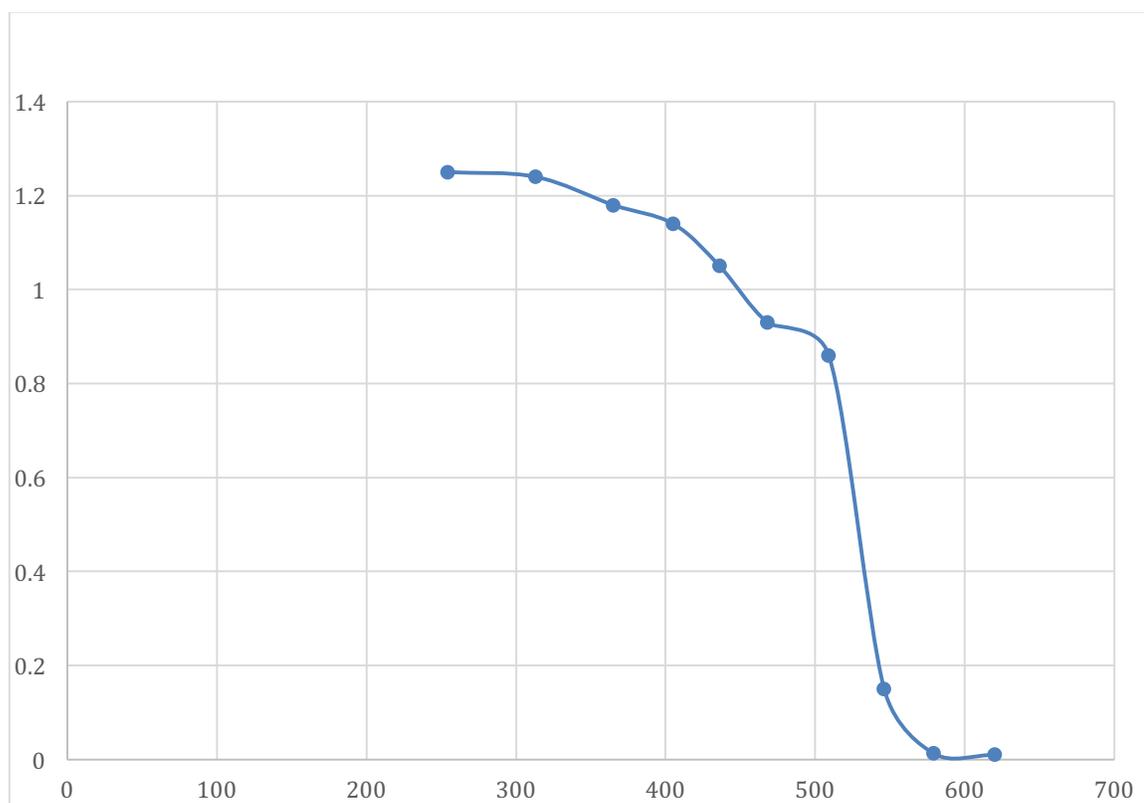


Fig. 12.2 Quantum Yields ϕ for the Photolysis of aqueous $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$

The figures plotted in the graph, are given in Table 12.2 below. Wavelengths λ , correspond to the major lines in the atomic emission spectrum of mercury.

λ/nm	254	313	365	405	436	468	509	546	579	620
$\phi/\text{mol Fe}$	1.25	1.24	1.18	1.14	1.05	0.93	0.86	0.15	0.01	0.0

Table 12.2 Quantum yield ϕ for $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ at various Hg wavelengths λ

In contrast with the data measured for the aqueous solution, the determination of ϕ for trisoxalatoferrate(III) in the solid state is beset with difficulties arising from geometrical–optical effects and the physical state of the sample. Values of ϕ ranging from 0.15 to 1.3 at 365 nm have been reported⁸¹⁶ and the origins of these seemingly discordant results have been discussed in some depth; a value of $\phi = 0.68$ at 365 nm seems most reliable.⁸¹⁷ It is also significant that ϕ has been found to be sensitive to the presence of oxygen;⁸¹⁸ it is therefore important that the exposing paper should not have uneven access to the atmosphere when in its printing frame. We see that between 300 and 500 nm the quantum efficiency does not vary very much, and it is the least important factor in determining the variation of yield with wavelength. The response of siderotype coatings (e.g. chrysotype, cyanotype or platino–palladiotype) is different intrinsically from that for photohardening of dichromated colloids (e.g. gum bichromate and carbon printing). There will even be differences between iron–based processes using different iron complexes.

12.3 Absorbance of the photoactive species



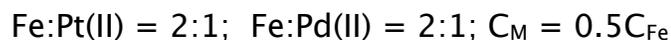
Fig. 12.3 The UV–visible absorption spectrum of $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$

This is determined partly by the absorption spectrum of the trisoxalatoferate (Figure 12.3) but it must also take account of any ‘internal filter effect’: many alternative process sensitive coatings also contain coloured substances that do not contribute significantly to the light-sensitivity (i.e., the pigment in gum bichromate and carbon; the potassium ferricyanide in cyanotype; the noble metal salts in platino-palladiotype). These substances absorb the printing light as it passes through the coating, and give nothing in return (on the assumption that there is no energy transfer). The presence of these coloured (and UV-absorbing) substances is like the effect of a coloured filter over the light source – except that the filter is ‘built-in’, and inescapable. This is called the ‘internal filter effect’ and it may be quantified using the Beer-Lambert Law. The internal filter effect is substantially absent in iron-silver sensitizers, and gold(I).

For a two-component system, in which ϵ_{Fe} and C_{Fe} denote the molar absorptivity and concentration of the photoactive component, trisoxalatoferate(III), and ϵ_{M} and C_{M} denote the same parameters for the inert filter substance, the metal salt, the total optical density D of the layer, assuming the Beer-Lambert law holds,⁸¹⁹ is:

$$D = (\epsilon_{\text{Fe}}C_{\text{Fe}} + \epsilon_{\text{M}}C_{\text{M}})d$$

where d is the layer thickness in cm. The concentration C_{M} of the metal salt is related to C_{Fe} the concentration of the trisoxalatoferate(III), in the sensitizers used here, by the stoichiometry of the redox reaction:



The fraction of incident light absorbed in total by the layer of sensitizer is then given by the Beer-Lambert Law:

$$(I_0 - I_t)/I_0 = 1 - 10^{-D}$$

but the fraction of incident light absorbed by the photoactive component *only* in the sensitized layer is a proportion of this given by:

$$f = (1 - 10^{-D}) \epsilon_{\text{Fe}}C_{\text{Fe}}d/D$$

f is strongly wavelength-dependent due to the steeply falling extinction coefficient of the trisoxalatoferate(III) absorption spectrum with wavelength. In those sensitized layers where the metal salt has an intense absorption spectrum, there is additionally the ‘internal filter’ effect. Knowing the absorption spectra (in terms of their molar extinction coefficients) of the two components, trisoxalatoferate and metal salt, and the molar coating weight W of the sensitizer, f can be calculated at various wavelengths, as shown in Table 12.3. The molar coating weight, W , of photosensitive iron complex is given by the molarity of the iron in the coating solution ($[\text{Fe}] = 0.7 \text{ M}$ for Pt-Pd sensitizers, but ca. 0.16 M for gold sensitizers) multiplied by its specific coating volume in units of $\text{dm}^3 \text{ m}^{-2}$ (0.024 for a typical paper absorptivity), so:

$$W = 0.7 \times 0.024 = 0.0168 \text{ mol m}^{-2} \text{ for Pt-Pd}$$

$$W = 0.16 \times 0.024 = 0.00384 \text{ mol m}^{-2} \text{ for Au}$$

The concentration C_{Fe} in mol dm⁻³ multiplied by the effective optical path length, d , in cm is related to the coating weight, W , by:

$$C_{\text{Fe}}d = 0.1W = 0.00168 \text{ cm mol dm}^{-3} \text{ for Pt-Pd}$$

$$C_{\text{Fe}}d = 0.1W = 0.000384 \text{ cm mol dm}^{-3} \text{ for Au}$$

The factor of 0.1 is included to take account of the units (cm) customarily used for d in the definition of molar extinction coefficient ϵ .

Wavelength	Quantum Yield	Fraction of light, f ,	
(Hg lines)	(per mol of Fe)	absorbed by $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$	
λ/nm	$\phi/\text{mol/einstein}$	in PtCl_4^{2-}	in PdCl_4^{2-}
254	1.25	0.94	0.76
313	1.24	0.99	0.89
365	1.18	0.92	0.90
405	1.14	0.35	0.32
436	1.05	0.073	0.063
468	0.93	0.0078	0.0022
509	0.86	0.00084	0.00043
546	0.15	0.00048	0.00048
579	0.013	0.0011	0.0011
620	<0.01	0.0022	0.0022

Table 12.3 Fraction of light absorbed by sensitizers with wavelength.

These considerations will not apply exactly to sensitizers containing ferric oxalate, which has a somewhat different absorption spectrum to that of trisoxalatoferrate(III), but has not, understandably, been accurately investigated and reported, due to the ill-characterised nature of this salt.

12.4 Absorption of UV by glass

How much UV radiation at each wavelength is actually arriving at the surface of the print depends on the transmittance of the glass of the printing frame. The following table gives for your guidance the UV absorption of windowglass of various thicknesses, so you can assess the light loss in relation to the wavelength emission of any UV source:

Glass Thickness	Wavelength in nm for transmittance	50%	30%	10%
1 mm		316	312	307
3 mm		330	323	314
10 mm		352	342	330

Table 12.4 Absorption of UV light by ordinary (window) glass.

Perspex and white crown glass absorb similarly. Pyrex absorbs slightly less.

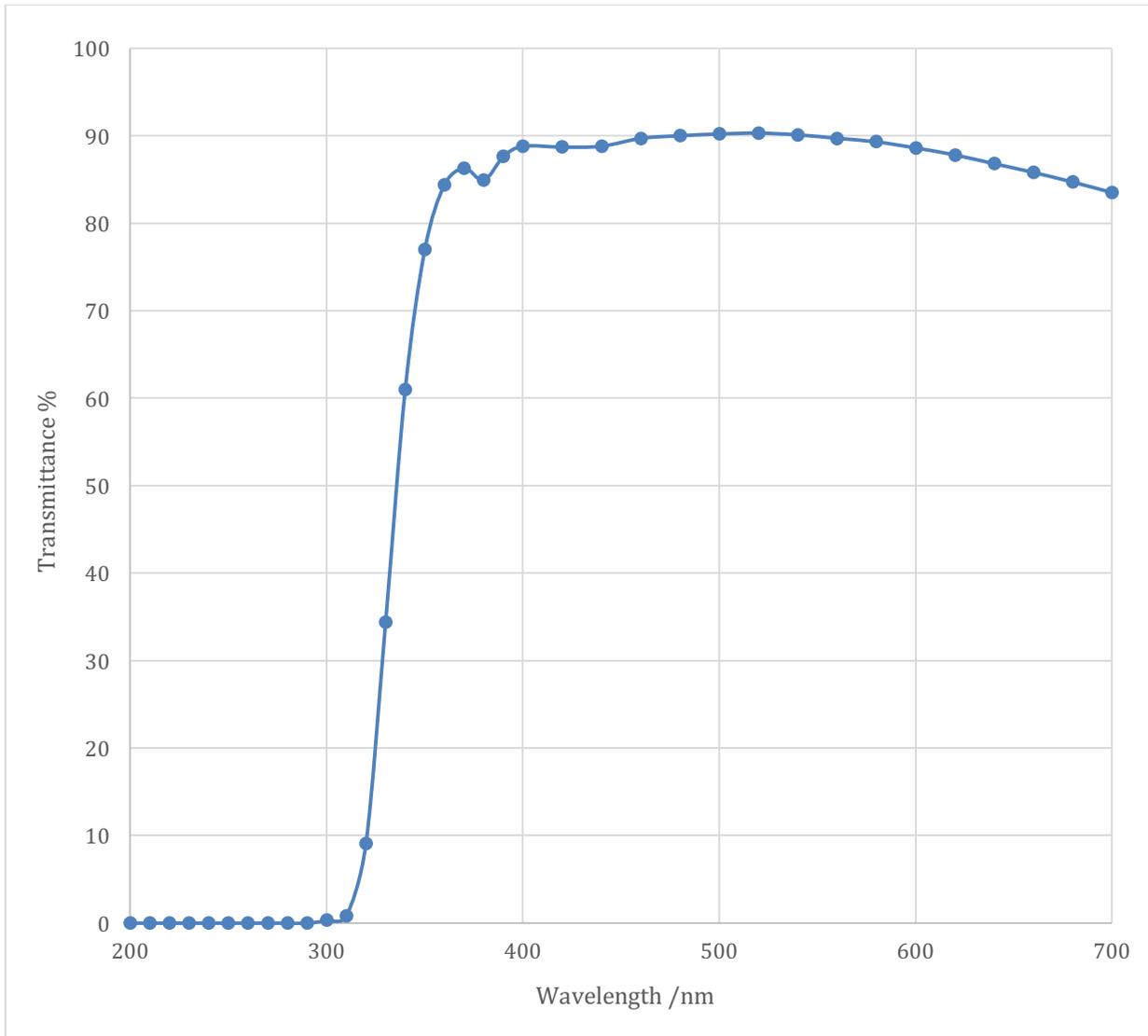


Fig. 12.4 Transmittance of typical clear glass 4 mm thick

Additionally, any other UV absorbing material in the path, even if apparently clear, can absorb an important part of the actinic light; e.g. plastic masks, and the negative film base itself, which may have a cutoff in the UV.

12.5 Wavelength dependence of photochemical yield

All these factors come into play in deciding the overall response of iron-based printing: this qualitative fact has long been known.⁸²⁰

λ nm	$\phi(\text{Fe})$	f(Pt)	f(Pd)	f(Au)	Tglass	Lamp I	Yield Pt	Yield Pd	Yield Au
280	1.24	0.9946	0.8637	0.6605	0.000	0.0000	0.0000	0.0000	0.0000
300	1.24	0.9948	0.8837	0.6023	0.003	0.0029	0.0010	0.0009	0.0016
320	1.23	0.9853	0.8825	0.5483	0.091	0.0489	0.0312	0.0296	0.0473
340	1.21	0.9779	0.9262	0.4790	0.610	0.1897	0.2172	0.2174	0.2897
360	1.20	0.9378	0.9140	0.3563	0.844	0.2644	0.3027	0.3117	0.3131
380	1.17	0.6743	0.6502	0.1992	0.849	0.2414	0.2253	0.2295	0.1812
400	1.15	0.3995	0.3644	0.1164	0.888	0.1466	0.1445	0.1392	0.1146
420	1.10	0.1525	0.1313	0.0382	0.887	0.0575	0.0553	0.0503	0.0377
440	1.05	0.0482	0.0421	0.0114	0.888	0.0316	0.0175	0.0161	0.0113
460	0.95	0.0094	0.0086	0.0022	0.897	0.0144	0.0033	0.0031	0.0021
480	0.92	0.0041	0.0039	0.0010	0.900	0.0029	0.0015	0.0014	0.0009
500	0.88	0.0011	0.0011	0.0003	0.902	0.0000	0.0004	0.0004	0.0002
520	0.66	0.0004	0.0004	0.0001	0.903	0.0000	0.0001	0.0001	0.0001
540	0.25	0.0004	0.0004	0.0001	0.901	0.0000	0.0000	0.0000	0.0000
560	0.06	0.0006	0.0006	0.0001	0.897	0.0000	0.0000	0.0000	0.0000
580	0.01	0.0010	0.0010	0.0002	0.893	0.0000	0.0000	0.0000	0.0000
600	0.01	0.0015	0.0015	0.0004	0.886	0.0000	0.0000	0.0000	0.0000

Table 12.5 Wavelength variation of quantum efficiency & the fraction of light absorbed and relative yield of noble metal sensitizers.

Since the yields of Pt and Pd pass through a maximum around 360–370 nm, the best choice of a suitable lamp for printing is one having peak spectral emissivity around 365 nm, e.g. the Philips actinic/05. The UV absorption of glass, present in nearly all systems, sets a short-wavelength limit of ca. 320 nm, where the steeply falling intensity is down to <10% for a 4 mm thick sheet. The “internal

filter effect" sets an effective upper wavelength limit of 430 nm. So most (ca. >90%) of the action in Pt/Pd printing occurs within the wavelength range 320–430 nm, see Table 12.5.

- λ = wavelength in nanometers
 $\phi(\text{Fe})$ = quantum yield of $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$
 $f(\)$ = fraction of incident light absorbed by a typical sensitizer for platinum (Pt), palladium (Pd), or gold (Au)
 T_{glass} = transmittance of a 4mm thick sheet of clear glass
 Lamp I = relative emissivity of a Phillips actinic/05 UVA lamp
 $\text{Yield}(\)$ = $\lambda\phi fT$ = relative yield of photoproduct noble metal, not scaled for Lamp intensity distribution

12.6 Theory of exposure times

Using the laws of photochemistry summarised in §13, a theoretical relationship between the exposure and the other parameters of the system can now be derived:

Over an area, A , of sensitizer during an exposure, t
 total energy absorbed by the photoactive component = $ItfA$

Now, the energy per photon = hc/λ
 so for the photoactive component:

$$\text{number of photons absorbed} = ItfA\lambda/hc$$

If m is the number of moles of photoactive component reacted:

$$\text{number of molecules reacted} = Nm$$

where N is Avogadro's number.

Recalling the definition of the quantum yield, ϕ :

$$\phi = \text{no. of molecules reacted} / \text{no. of photons absorbed}$$

$$\phi = Nmhc/ItfA\lambda$$

Rearranging this equation we get:

$$It\phi f\lambda = Nhcm/A$$

Where the quantities on the LHS (except t) depend on wavelength λ as above:

I = irradiance in W m^{-2} at wavelength λ

t = exposure time in s

ϕ = quantum efficiency of the photoactive substance at wavelength λ

f = fraction of the incident radiation absorbed by the photoactive substance at wavelength λ as calculated and described under 3 above. (f is assumed, for simplicity, to be independent of the exposure – an assumption that will only be valid for small changes – *i.e.* formation of a 'just perceptible' image, or where there is no self-masking of the image).

λ = wavelength of radiation in m (assumed monochromatic)

$$N = \text{Avogadro's number} = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$h = \text{Planck's constant} = 6.626 \times 10^{-34} \text{ J s}$$

$$c = \text{speed of light} = 2.998 \times 10^8 \text{ m s}^{-1}$$

m = number of moles of photoproduct

A = area of normal surface irradiated in m^2

It is possible to use this relation to calculate the photochemical yield from any source by integrating over the whole waveband of the emission. However, by making a couple of approximations we can reach a rough estimate of the exposures needed.

If the waveband of useful available actinic light is taken as 300–430 nm, we may select a median value of the wavelength as $\lambda = 365$ nm, (corresponding with the atomic mercury line, and the maximum emission of most UVA lamps).⁸²¹

Then, inserting values for the physical constants, we have the value of one Einstein, which is the the energy of a mole of photons as:

$$Nhc/\lambda = 3.28 \times 10^5 \text{ J mol}^{-1} \text{ at } \lambda = 365 \text{ nm}$$

Moreover, assuming optimum conditions for the absorption of actinic light by setting $\phi = f = 1$ approximately (see values in Table above), we get the simple relation between exposure in J m^{-2} and yield of photoproduct in mol m^{-2} :

$$It = 3.28 \times 10^5 \text{ m/A J m}^{-2}$$

This assumes that:

(i) only the $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ is photoactive, and that no energy transfer takes place from the platinum metal complex

(ii) the Beer–Lambert absorption law is valid in a heterogeneous system of metal ions absorbed on cellulose

(iii) there is no significant loss by scattering or absorption due to the other components of the sensitized paper.

If it is further required that all the photoproduct be converted into image pigment;⁸²² to yield the maximum optical density, the molar yield per unit area must be equal to the original coating weight, W , of the sensitizer, estimated in (3) above:

$$m/A = W = 0.0168 \text{ mol m}^{-2} \text{ for Pt–Pd or } 0.00384 \text{ mol m}^{-2} \text{ for Au}$$

$$\text{Whence } It = 5510 \text{ J m}^{-2} \text{ for Pt–Pd or } 1259 \text{ J m}^{-2} \text{ for Au}$$

For a typical UVA source delivering 50 W m^{-2} at the print surface, see §6.13 and §7.19, bearing in mind that $1 \text{ W} = 1 \text{ J s}^{-1}$, the times required to make full exposures of such sensitizers (with zero intervening density) are therefore predicted to be

$$5510/50 = 110 \text{ s or ca. two minutes for Pt–Pd}$$

$$1259/5 = 25 \text{ s or ca. half a minute for Au}$$

These predictions are born out well in practice, allowing for the optimistic assumptions that have been made in the theoretical calculation. A more exact calculation was also performed, in which the product $I\phi\lambda$ was integrated over the entire waveband of the light source emission, but it gave a result only slightly larger, ca. 150 seconds, for the exposure.

APPENDIX I

Introduction to Relevant Photochemistry

1.1 Oxidation and reduction exemplified by iron

When iron (symbol Fe, from the Latin *ferrum*) is chemically combined with other elements, it usually ends up in one or the other of two possible states:

either "ferrous" iron, also called iron(II) ["iron-two"] and symbolised by Fe²⁺ or "ferric" iron, also called iron(III) ["iron-three"] and symbolised by Fe³⁺.

These superscripted numbers 2+ and 3+ are the **oxidation states** of the iron, signifying the positive electric charge that the iron atom – originally neutral – has acquired from the reaction by losing negatively-charged electrons from the outermost regions of the atom. So:

Oxidation is making an atom or molecule more positive (or less negative) in the electrical sense. When iron forms compounds, it is oxidized.

Reduction is the converse: making an atom or molecule less positive (or more negative). *e.g.* oxygen gas (O₂) is reduced to form oxides, which contain the oxide anion O²⁻.

Both processes involve the transfer of electrons, which are the fundamental particles of negative electricity and make up the outer spheres of all atoms.

Positively-charged atoms or molecules are called **cations**

Negatively-charged atoms or molecules are called **anions**

Chemistry is governed by the redistribution of electrons between atoms.

Oxidation is the removal of electrons – formation of cations

Reduction is the addition of electrons – formation of anions

The number of electrons must always balance to zero net charge overall.

Iron is easily oxidized: for example, it rusts to form iron(III) oxide, Fe₂O₃ and consequently iron is said to be **electropositive**. In contrast to iron, metals such as platinum, palladium and gold are very resistant to oxidation, don't rust or even tarnish, and are designated as **noble**.

Atoms that strongly attract electrons are said to be **electronegative**, such as oxygen and the halogens (fluorine, chlorine, bromine and iodine).

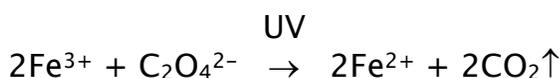
NB: in chemical formulae, the subscripted numbers give the relative number of such ions or atoms present, and **charges always balance** in a neutral molecule. Thus in Fe₂O₃ :

$$2 \times (+3) + 3 \times (-2) = 0$$

1.2 Iron-based imaging systems

The key compound is light-sensitive ferric oxalate, formula Fe₂(C₂O₄)₃, which contains ferric cations Fe³⁺ and oxalate anions (C₂O₄)²⁻ chemically bound together. Under the influence of ultra-violet (UV) light, these two ions undergo a reduction-oxidation reaction, which can be summarised in words as:

"Under UV light, ferric cations (iron(III)) react with oxalate anion to give ferrous cations (iron(II)) and carbon dioxide gas" so we can now "read" this chemical reaction when it is written symbolically as a chemical equation:



ferric cations + oxalate anion → ferrous cations + carbon dioxide gas

NB: in chemical equations, the large + signs simply mean "...added to..." or "...mixed with.." (they have nothing to do with electric charges) and the horizontal arrow → means "...react chemically to give the products...".

Written above → is the source of energy promoting this reaction: UV light. The use of an arrow implies that the reaction effectively "goes to completion" and there is a negligible amount of the starting materials on the left hand side remaining. The use of an equals sign, =, instead of an arrow, implies a chemical equilibrium, where both starting materials and products have significant final concentrations.

The upwards arrow ↑ on carbon dioxide means "...is evolved as a gas".

NB: the reaction has transferred two electrons (negative charges) from one oxalate anion, to two iron(III) cations, keeping the number of electrons balanced in this chemical equation, because opposite charges neutralise or cancel one another. The chemical reaction has been dissected in this way, so you can see the oxidation–reduction process in principle. The actual equation for the photochemical reaction in the solid is usually written like this:

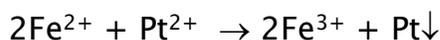


ferric oxalate → ferrous oxalate + carbon dioxide gas

This light–induced change occurs in solid ferric oxalate, to give solid ferrous oxalate; but there is only a slight color change (from pale yellow–green to pale yellow–brown), and the result is not permanent, because the oxygen of the air will eventually re–oxidise the iron(II) back to iron(III). To make a satisfactory photographic image, the iron(II) oxalate which is formed by the UV light must be reacted promptly with something else. Now, iron(II) is a reducing agent, because it readily gives up an electron and reverts to iron(III); so it can be used to reduce the compounds of a noble metal to the metallic state, as we shall see next.

1.3 Classical platinum and palladium printing

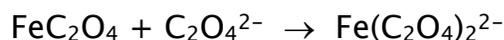
This is the two stage process of 'development' platinum printing, as described in the 19th century literature. The traditional platinotype sensitizer consists of a mixture of aqueous (*i.e.* water) solutions of ferric oxalate and potassium chloroplatinite, which we now prefer more accurately to call potassium tetrachloroplatinate(II), formula K_2PtCl_4 , and which contains platinum in the oxidation state +2. The iron(II) formed as described above by the exposure to UV light is capable of reducing the platinum(II) to its solid metallic state, which is oxidation state zero (the 0 is not usually written):



iron(II) cations + platinum(II) → iron(III) cations + platinum metal

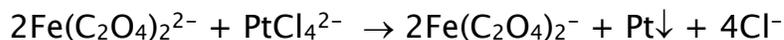
The downwards arrow ↓ means "precipitated as a solid". Note that it takes two iron(II) cations to make one atom of platinum, because two electrons are needed to balance the charges on each side of the equation. These ratios are important in formulating the sensitizer solution correctly. This is again a 'dissected' version of the chemistry; the actual molecules involved are complex, as we'll see in a moment.

However, this second reaction cannot take place in the dry sensitizer, because the ions (charged atoms or molecules) are immobile in the solid and cannot encounter one-another. Only when dissolved in water are they freely mobilised to react. The problem is that the iron(II) oxalate produced by UV light is insoluble in plain water; so to dissolve it, the traditional "developer" uses a solution of the salt, potassium oxalate, $K_2C_2O_4$ which supplies oxalate anions which bind to, and dissolve the ferrous oxalate:



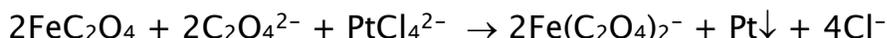
iron(II) oxalate + oxalate anion → bisoxalatoferate(II) complex anion

this solution of an iron(II) oxalato complex can then react with the soluble tetrachloroplatinate(II) to precipitate tiny particles of platinum metal, which appear black and are trapped in the paper fibres to constitute the final image:



bisoxalatoferate(II) + tetrachloroplatinate(II) → bisoxalatoferate(III) + platinum + chloride

The potassium ions, K^+ , don't come into it, and remain unchanged on both sides of the equation, so we usually omit them in writing the overall balanced equation for the "development" reaction like this:



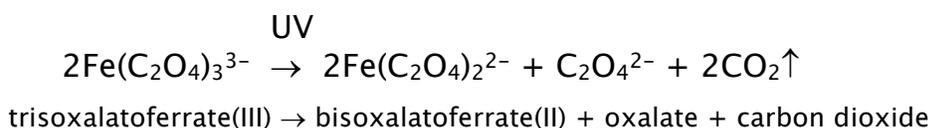
iron(II) oxalate + oxalate + tetrachloroplatinate(II) → bisoxalatoferate(III) + platinum + chloride

Finally, all the excess unreacted sensitizer chemicals and soluble reaction products are removed from the paper by baths of dilute (2%) hydrochloric acid, thus 'fixing' or, more accurately, 'clearing' the platinum image.

The closely-related element, palladium, Pd, reacts in a similar way.

1.4 Modern platinum-palladium printing

An alternative "printing-out" process, researched by Malde and Ware in the 1980s, can offer some advantages. With this method, the sensitizer is now composed of solutions of ammonium iron(III) oxalate, formula $(NH_4)_3Fe(C_2O_4)_3$, and ammonium tetrachloroplatinate(II), formula $(NH_4)_2PtCl_4$, or the analogous palladium compound. The sensitized paper is not fully dried but allowed to acquire a controlled degree of humidity prior to exposure. At normal relative humidity – around 70% – cellulose paper contains about 8% by weight of water. Under these conditions the platinum or palladium image is formed during the exposure, and requires little or no development afterwards. The light-induced reaction goes like this – the light-sensitive substance being now the ferrioxalate ion:



But the iron(II) reaction product on the right hand side of this equation is still soluble in water (unlike the traditional case), so if the paper is slightly humid it can react immediately with the platinum(II) salt exactly as shown by the equations above.

The traditional clearing agent of dilute hydrochloric acid tends to dissolve palladium and weaken the cellulose structure of the paper. A better modern reagent is disodium EDTA, short for ethylenediaminetetraacetate, which is effective in binding iron(III) strongly under mildly acid conditions, and removing it from the paper. Finally a water wash completes the processing, leaving an archivally permanent print.

1.5 Other siderotype processes

As alternatives to platinum and palladium, as described above, other noble metals have been used historically, e.g. gold (chrysochrome and aurochrome) or silver (argentochrome or kallitype) or even mercury (amphitype and celaenotype or kelainotype), with appropriate changes in the chemistry, although the principles are the same. Inexpensive methods are provided instead by reacting the iron(II) with ferricyanide (cyanotype, ferroprussiate or blueprint process) or gallic acid (ferrogallate 'Ink' process). In these methods, use is made of substances that form highly-coloured insoluble pigments with the iron. See §11.3.

Ferric oxalate and ammonium ferric oxalate are not the only light-sensitive iron(III) salts that can be used in siderotype sensitizers: other salts of organic acids, such as the citrate or tartrate, are also employed, e.g. in the silver processes called van Dyke, brownprint and argyrotypes, the complex salt, ammonium ferric citrate is used; this is somewhat less light-sensitive than the oxalate, and the photoproduct iron(II) citrate complex is a less powerful reducing agent than the iron(II) oxalate complex, so it cannot be used for platinotype.

1.6 Chelating ligands for clearing prints

First to demystify the jargon: "ligand" is one of the most heavily-used words in chemistry, and is very general. It means no more than its Latin origin suggests – something that "binds" – any atom, ion or molecule that can bond with a 'central' atom or ion, which is usually a metal. A ligand is usually thought of as donating one – or more – pairs of electrons to the metal. In the chemistry described above, both the chloride anion Cl^- in PtCl_4^{2-} and the oxalate anion $\text{C}_2\text{O}_4^{2-}$ in $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ are ligands. When a ligand employs two (or more) points of attachment – *i.e.* donor atoms – then it is called a "chelating ligand" and the resulting complex is called a "chelate".

Such a ligand is more effective in binding to a metal than a monodentate ligand, having only one donor atom. The oxalate anion is a simple chelating

ligand, usually exercising two oxygen atoms as electron pair donors, so is called a 'bidentate' chelate.¹⁰

More complex chelating agents such as EDTA, can occupy up to six coordination positions. See §10.9.

1.7 Summary of photochemical principles

There are five basic 'Laws' relating to photochemical processes; they are not all rigorously obeyed, but are sufficiently valid to be useful for understanding the behaviour of light-sensitive substances, and for approximate calculations.

1.8 Grotthuss-Draper law

Photochemical theory had its beginnings with the Grotthuss-Draper Law (*ca.* 1818), which is a commonsense statement that, for light to have any effect on matter, it must first be absorbed:¹¹

**Only the light absorbed by a substance
may induce a chemical change within it**

Light is a form of energy. Across the visible spectrum, in going from red to blue, the intrinsic energy of the light nearly doubles (see Planck's Law below). When a molecule absorbs a photon of light (visible or UV), its internal energy is increased, and it is said to be lifted into an 'excited' state. Sooner or later, this excitation energy is transformed and lost, so that the molecule returns to its normal or 'ground' state. This process is appropriately called 'relaxation'. The manner of the transformation of the absorbed energy, however, can be various, and it depends on the lifetime of the excited state and other factors. The least interesting, and most common process is 'thermal relaxation', that is the dissipation of the excess energy as heat which is manifested as more agitated motion of the molecules. More interestingly, in some spectacular cases, part of the excess energy may be re-emitted as light, giving us the attractive and useful luminescent phenomena, which are called fluorescence and phosphorescence, depending on whether the excited state is short- or long-lived, respectively. Most importantly for our purposes, the excess energy may bring about a chemical reaction if the molecular circumstances are favourable. It should come as no surprise that a molecule in an excited state is capable of more vigorous chemical reactions than when in its ground state. Ultra-violet light is often required to supply sufficient energy for such chemical transformations.

¹⁰ *Etymological footnote 10: The word "chelate" derives from the Greek for a crab's claw "chele" = χηλη, offering a visual analogy for the manner of the molecule's binding to a metal ion in a 'pincer action'. A 'bidentate chelate' mixes both metaphors and classical roots: a Greek crab's claw having two Latin teeth!*

¹¹ *Eponymical footnote 11: German chemist Freiherr Christian Johann Dietrich Theodore von Grotthuss (1785-1822) was born in Leipzig. Scientist and philosopher John William Draper (1811-1882) was born in St. Helens, England, but emigrated to the USA and by 1838 was professor of chemistry at New York University. He has a number of photographic "firsts" to his credit: the first portrait, the first astrophotograph, and the first detailed picture of the moon.*

1.9 Stark–Einstein law

There is an equivalence between the quantity of light absorbed and the amount of substance that is chemically transformed, both of which are measurable, and may be related by an elementary principle of quantum theory, as it applies to photochemical changes.⁸²³ This principle dates from *ca* 1912 and is usually referred to as the Stark–Einstein Law,¹² which effectively requires that:

**For each molecule to be transformed
one photon must be absorbed**

It is easily appreciated without invoking much jargon, and the non-technical reader should readily see that it amounts to nothing more than a statement of ‘good book-keeping’ at the molecular level. A photon is the fundamental, indivisible particle or *quantum* of light.

The extent to which this ‘Law’ is obeyed may be quantified by defining the quantum yield, given the symbol Greek ‘phi’ ϕ as:

$$\phi = \text{number of molecules reacted} / \text{number of photons absorbed}$$

When $\phi = 1.000$, the Stark–Einstein Law is obeyed exactly. Apparent departures from $\phi = 1$, significantly greater than one, arise when the primary light reaction triggers secondary reactions; this is the case in iron–oxalate photochemistry, where one photon leads to the reduction of two ions of Fe(III) as may be seen in the equations above: here ideally $\phi = 2$. The quantum yield can quite commonly appear to be less than ideal, however, due to competing reactions which diminish the efficiency of the photochemical process.

1.10 Planck law

There is an equivalence between the energy, E , of a photon and the frequency, ν , (Greek *nu*) of the radiation, as given by the quantum theory of Max Planck:

**The energy of a photon is directly
proportional to the frequency of its wave**

$$E = h \nu \quad \text{Joules (J)}$$

The constant of proportionality h is Planck's constant:

$$h = 6.626 \times 10^{-34} \quad \text{Joule seconds (J s)}$$

The frequency, ν , and wavelength, λ , of electromagnetic radiation are related by the speed of light, c :

$$\nu \lambda = c = 2.998 \times 10^8 \quad \text{meters per second (m/s)}$$

¹² *Eponymical footnote 12: German physicist Johannes Stark (1874–1957) won the Nobel prize for physics in 1919. However, his scientific distinction was not matched by his ethics: during the Third Reich he acted as a conspicuous Nazi propagandist, denouncing the "Jewish physics" of Einstein in the SS Newspaper ‘Das Schwartzte Korps’. Ironically, in this photochemical law, Stark's name is indissolubly wedded to that of his primary hate-object, Albert Einstein.*

1.11 Bunsen–Roscoe law

This ‘Law of Reciprocity’ is enshrined in the definition of light exposure, H , as equal to the light intensity, I , multiplied by the duration, t , of the exposure:¹³

$$H = I t \quad \text{lux seconds (lx s)}$$

**In photochemical exposures there is reciprocity
between light intensity and exposure duration**

Thus, for a given exposure, the intensity is proportional to the reciprocal of the time, and *vice versa*. This relation only has a limited range of validity, for a variety of reasons: for very high or very low light intensities, the exposure times required to produce the same effect as that of average light intensity are longer than the definition would predict. This non-compliance is called ‘reciprocity failure’ and is a property of camera film familiar to any practising photographer.

1.12 Beer–Lambert law

This refers to the absorption of monochromatic light passing through a homogeneous medium:¹⁴

**The optical density, D , is directly proportional to the
molar concentration, C , and the path length, d :**

The constant of proportionality, the molar extinction coefficient, ϵ , (Greek *epsilon*) is also called the *molar absorptivity* for a given substance, and has (non-SI) units of cubic decimeters per mole per centimeter ($\text{dm}^3/\text{mol}/\text{cm}$):

$$D = \epsilon C d$$

where the path length d is given in cm and D is without units. ϵ varies with wavelength, which should always be specified. In terms of the intensities of light, incident I_0 and transmitted I_t , by the sample, it may be shown that:

$$D = \log_{10} (I_0 / I_t) \quad \text{or} \quad I_t / I_0 = 10^{-D}$$

¹³ *Eponymical footnote 13: British inorganic chemist Sir Henry Enfield Roscoe (1833–1915) studied with the distinguished German physicist and chemist Robert Wilhelm Bunsen (1811–1899), and became professor at The Victoria University of Manchester.*

¹⁴ *Eponymical footnote 14: This law was not discovered by the German physicist August Beer (1825–1863) of Trier, in 1852, nor by the Swiss mathematician Johann Heinrich Lambert (1728–1777) of Mulhouse, in 1760 (after whom is named the c.g.s unit of photometric luminance, the lambert). The origins of the so-called Beer–Lambert law can be traced to French hydrographer and geodesist, Pierre Bouguer (1698–1758) whose ‘Essai d’optique sur la gradation de la lumière’ (1729) laid the foundations of photometry. In 1735 he sailed with French explorer and geographer, Charles Marie de la Condamine (1701–1774) to South America on the same scientific expedition that included Don Antonio de Ulloa, the “discoverer” of platinum – see §1.1.*

APPENDIX II

Technical Objectives of the NGA Project 2010–2015

1. Infer the likely composition of William Willis's Platinotype papers of 1892 on, and 'Palladiotype' papers of 1917–35, by historical research and chemical and spectroscopic analysis of original specimens that have so far come to hand: 'KK' and 'AA' Platinotype paper, and 'Sepia Japine'; also American Aristotype, and Eastman Kodak 'WD' paper.
2. Investigate the surfaces of Stieglitz's 'semi-glossy' Palladiotype and Platinotype prints by infrared spectroscopy and cross-section microscopy to study their laminar structure and determine if they are coated. Try to establish the nature of Willis's 'Japine' surfaced papers, and decide which Stieglitz photographs were printed on them.
3. Re-create similar platinum and palladium printing papers, both 'matt' and 'Japine' using appropriate sensitizer formulae and paper stock – modifying the surface, if necessary, to mimic the characteristics of NGA prints, by 'parchmentising' with concentrated sulphuric acid.
4. Print test platinum and palladium images, as simulacra, and process them, both in the recommended developing and clearing agents (UK tradition – Willis) and the agents generally used for Platinotype (US tradition – Anderson).
5. Endeavour to produce yellow-stained images by deliberately curtailed or 'negligent' processing, à la Stieglitz, and by 'humid' storage before exposure.
6. Explore the effect of ambient conditions of relative humidity and paper type on the image colour, tonal scale, and staining of the platinum and palladium print, with particular reference to the conditions for producing 'reversal'.
7. Conduct accelerated ageing tests on stained Palladiotype and Platinotype simulacra for comparison with controls. Carry out measurement of colour change/UV-visible absorption spectra of stain.
8. Conduct spectroscopic investigations into the chemical nature of the yellow stain (including the shadow areas where it may be 'invisible') by: UV/visible spectrophotometry; infra-red and Raman spectroscopy; various X-ray spectrometries, and possibly magnetic measurements – SQUID and electron paramagnetic resonance spectrometry, especially with regard to the speciation of the iron present.
9. Test modern stain-removing treatments on Palladiotype and Platinotype simulacra: dithionite/EDTA; metabisulphite/HF; also try ascorbic acid as reductant plus EDTA and stronger chelating agents, such as CDTA and DTPA. Subject treated specimens to re-ageing, for stain recurrence.

APPENDIX III

Chronology of Platinotype & Palladiotype

- 1741 A specimen of platinum, acquired in Jamaica, is brought back to England by metallurgist Charles Wood who performs preliminary tests upon it
- 1748 Platinum metal, long-known in South America, is introduced into Europe by Spaniard Don Antonio de Ulloa via the French scientific expedition to Ecuador and Colombia in 1735
- 1802 Palladium metal discovered by William Hyde Wollaston (1766–1828), inventor of the *camera lucida*
- 1804 Adolph Ferdinand Gehlen (1775–1815) observes that platinic chloride dissolved in ether is sensitive to light
- 1819 Platinum discovered in the Eastern slopes of the Urals
- 1825 Russia declares platinum a State monopoly
- 1826 Johann Wolfgang Döbereiner (1780–1849) precipitates platinum from a solution of platinic chloride and sodium tartrate by the action of sunlight
- 1831 Döbereiner notes light sensitivity of ferric oxalate, also the light-induced precipitation of platinum metal from platinic chloride and oxalic acid
- 1832 Sir John Frederick William Herschel (1792–1871) reports the light-induced precipitation of "platinate of lime" from neutralised platinic chloride (a photoaquation reaction of the hexachloroplatinate(IV) anion to produce insoluble calcium hexahydroxoplatinate(IV))
- 1840 Herschel tests effect of light on paper impregnated with hexachloroplatinate(IV) finding a negative result, but added hydriodic acid gives light sensitivity (possibly by formation of iodine)
- 1842 Herschel describes in a paper to the Royal Society the use of ammonium iron(III) citrate and tartrate for the siderotype (iron-based) systems of imaging: cyanotype, argentotype, chrysotype, amphitype or kelainotype (a mercury print), but no mention of platinotype or palladiotype
- 1844 Robert Hunt (1807–1887), in *Researches on Light*, describes images formed by light on "a percyanate of potassium and platinum" developed by mercury(I) nitrate, which he calls "platinotypes"; these slowly fade in the dark and were probably composed of mercury. Also that ferrous oxalate plus hexachloroplatinate(IV) shows a (temporary) response to light
Hunt also notes the use of iron(III) oxalate for making prints in silver, anticipating the kallitype process of 1889 and other derivative iron-silver processes
- 1853 Hermann Halleur publishes the use of ammonium iron(III) oxalate as a photosensitive salt for making prints in Prussian blue, silver, and gold
Charles John Burnett (1820–1907) reports his use of uranium salt photochemistry to the British Association for the Advancement of Science

- 1856 Ernest de Carranza publishes a platinum toning formula for silver prints
Burnett exhibits platinum-toned silver prints at Edinburgh
- 1857 Burnett exhibits first palladium prints (made by a uranium(VI) sensitizer)
- 1871 First convenient preparation of potassium tetrachloroplatinate(II) by reduction of potassium hexachloroplatinate(IV) with sulphur dioxide (Blomstrand)
- 1872 William Willis (1841–1923) of Bromley, Kent makes first printing experiments with platinum(IV) salts and ferric oxalate, with poor results
- 1873 Willis succeeds with platinum(II) salts and takes out first British patent (no. 2011) for platinum printing (lead & silver salts added)
- 1876 Willis's US patent (no. 173381 8th February) as the 1873 British patent, but no mention of added silver
- 1877 Willis visits the USA and makes the first platinotype there (still containing gold & silver, now in GEM). He also forms a partnership with Alfred Clements, previously employed by his father
Preparation of potassium tetrachloroplatinate(II) by reduction of potassium hexachloroplatinate(IV) with copper(I) chloride (Thomsen)
- 1878 Willis makes first platinum print without added silver (now in MMA NY)
Willis's second British patent (no. 2800): no silver in sensitizer (but tetrachloroplatinate(II) in the developer as well as in paper); sepia platinotype using mercury salts. Possible use of palladium in sensitizer
Willis founds the Platinotype Company of London
- 1879 Willis's first Platinotype papers marketed
First book published illustrated with platinotypes
- 1880 Willis's third British patent (no. 1117): (no lead or silver, more platinum in coat, none in developer bath). No mention of palladium
Alfred Clements in New York making enlarged platinotypes with electric light but suffers a serious boiler explosion
- 1881 Royal Photographic Society awards William Willis its Progress Medal
Alfred Clements relocates the Willis & Clements Company to Philadelphia, retailing chemicals and paper for self-coating; Willis visits Philadelphia
- 1882 Giuseppe Pizzighelli (1849–1912) and Arthur Freiherr von Hübl (1853–1932) publish formulae for making platinum paper in *Die Platinotypie*, also describe successful brown prints in palladium, but not further used
The Platinotype Company markets the first sulphite/pyro developer
- 1883 Pizzighelli & Hübl's *Platinotype* translated into English (Iselin) and published in the *Photographic Journal*

- 1885 The Platinotype Company awarded a gold medal of the International Inventions Exhibition
- 1886 Alfred Stieglitz (1864–1946) practising platinotype in Germany under Prof. Hermann Wilhelm Vogel (1834–1898)
- 1887 Willis's fourth British patent (no. 1681): (platinum entirely in phosphate developer bath)
- Willis's fifth British patent (no. 16003): Lead &/or mercury essential in the sensitizer; platinum in the oxalate developer – the "Cold Bath" process
- Pizzighelli discovers a platinum 'printing-out' formula and markets a print-out paper ('water developed') – used by Stieglitz
- Peter Henry Emerson (1856–1936) publishes *Life and Landscape on the Norfolk Broads*: a document/artwork illustrated with 40 photographs by himself and T.F. Goodall, printed as original platinotype plates by James Valentine and Son of Dundee
- 1888 Willis & Clements in Philadelphia begin to import Platinotype Company sensitized papers into the USA
- Henry Peach Robinson (1830–1901) platinotype exhibition prints
- 1889 Frederick Henry Evans (1853–1943) begins his great cathedral studies, printing only in platinum
- 1890 Willis's US patent (no. 423849, 18th March) – same as 1887 British patent
- 1892 Willis announces 'Cold Development' platinotype paper (no patent) – all platinum in sensitizer – the perfected process
- 1893 William Willis – 'glycerine development' of platinotype
- 1895 Arthur Freiherr von Hübl publishes *Der Platindruck*, Wilhelm Knapp Packham's 'Catechu Toner' for platinotype, and Chapman Jones' explanation for its action
- 1899 Josef Maria Eder (1855–1944) describes making brown platinotypes with added palladium and mercury
- Iford Ltd., of London market a platinum paper "Platona".
- 1900 Evans' first RPS show of 150 platinotypes
- 1901 Kodak market their first platinum paper – American Aristotype Co.
- 1902 Friedrich Wilhelm Ostwald (1853–1932) patents use of platinum catalyst for oxidation of ammonia to nitric acid
- The Photosecession* founded by Stieglitz in USA: Steichen, Eugene, Coburn, Käsebier, White et al., printing in platinum and gum
- Second Edition of von Hübl's *Der Platindruck*, of 1895, revised to include use of palladium for sepia tones

- 1905 Sales of potassium tetrachloroplatinate(II) by Johnson–Matthey to the Platinotype Company reach a peak
Royal Photographic Society elects William Willis to Honorary Fellowship
- 1906 Eastman Kodak purchases di Nunzio of Boston
Willis markets 'Japine' (semi-glossy) platinotype paper
- 1913 Willis patents (no. 20022) a silver chloride–platinum paper (largely the former): 'Satista' – also used Japine surface
- 1914 World War I: platinum becomes a strategic material: catalyst for manufacture of sulphuric and nitric acids – needed to make nitrate explosives
Willis US patents (no. 1120429, 8th December, and 1120580)
- 1916 British Government prohibits the use of platinum for photography, jewellery, etc
First industrial plant in USA for platinum–catalysed oxidation of ammonia to nitric acid
Eastman Kodak discontinue manufacture of platinum papers
Evans gives up photography because of the non–availability of platinum paper
Paul Strand's platinum prints are published by Stieglitz in *CameraWork*
- 1917 Russian revolution – platinum resources nationalised
The Platinotype Company introduces a palladium printing paper: 'Sepia Japine Palladiotype' as a substitute for platinum
Alfred Stieglitz (1864–1946) begins his portraits of Georgia O'Keeffe (1887–1986) in platinum and palladium (chiefly); series continued until 1933
- 1918 Mrs Elwood B. Spear founds the *Women's National League for the Conservation of Platinum*, in Cambridge, Mass., with support of the American Chemical Society
The Platinotype Company markets 'Matt Palladiotype' paper
- 1920 Platinotype paper on the market once more in UK from the Platinotype Company, but price very high, (R. Child Bayley *The Complete Photographer*, 6th Edition)
- 1922 Platinotype Company announces reduction in platinotype paper prices
- 1923 Death of William Willis
- 1924 Platinotype Company Limited incorporated by its new proprietor John Willis, with Charles Robinson and Alfred Willis Clemes as directors
Russia resumes export of platinum to the West

- 1932 The Platinotype Co. Ltd. is wound-up as a private limited company
- 1937 The Platinotype Company sells last Platinotype and Palladiotype papers, then is dissolved voluntarily
Paul L. Anderson (1880–1956) republishes 1882 platinotype formulae of Pizzighelli & Hübl
- 1938 Commercial platinum papers are discontinued in the USA
Paul Anderson publishes and recommends recipe for palladiotype paper
- 1942 Karl Schumpelt patents palladium printing in the USA
- 1964 Irving Penn (1917–2009) begins experiments on printing in platinum metals, based on his research in NYPL on the early texts on platinotype
- 1970 George Tice revitalises interest in platinum printing in the USA by republishing in *Album* the 1937–8 recipes of Paul L. Anderson
- 1975 Irving Penn's first exhibition of a set of platinum–palladium prints of *Cigarettes* made in 1972, curated by John Sarkowski, at the Museum of Modern Art, NY
Laura Gilpin still hand-coating platinum paper as taught by Clarence White sixty years previously
- 1976 Alan Goodman founds *Elegant Images*, supplying platinum materials
- 1977 Nancy Rexroth, Smithsonian Institution, publishes *The Platinotype 1977*
Irving Penn exhibits large platinum–palladium prints of *Street Material* at The Metropolitan Museum of Art, NY
- 1979 William Crawford publishes *The Keepers of Light*, Morgan & Morgan, NY; John Hafey and Tom Shillea publish *The Platinum Print*, RIT, NY
- 1981 Bostick & Sullivan publish their *Labnotes* and *Catalogue*
- 1984 Luis Nadeau publishes *The History and Practice of Platinum Printing*
- 1985 Pradip Malde and Mike Ware begin platinum–palladium workshops in the UK and publish an up-dated, economic print-out process
- 1988 The Palladio Company in the USA re-launches commercial platinum–palladium paper, but folds again within a few years
Paul Caffell establishes *31 Studio* – the first 'latter-day' commercial platinum–palladium printing workshop in UK
- 2014 First major international conference on platinum and palladium printing, sponsored by the American Institute for Conservation of Historic and Artistic Works, Washington, DC
- 2017 Publication of *Platinum and Palladium Photographs: Technical History, Connoisseurship, and Preservation*, ed. Constance McCabe, Washington, DC: American Institute for Conservation of Historic and Artistic Works, 2017

APPENDIX IV

Preparation of Digital Negatives

IV.1 Summary and purpose

Herein follows a stepwise sequence of explicit instructions for making monochrome digital photographic negatives, using a personal computer and ink-jet printer, starting from original medium format camera negatives or transparencies, or from digital picture files. The software used for this image manipulation is Photoshop CS™ (Version 8) and Epson Scan, on an iMac, running OS 10.4. No additional software or 'latest upgrades' are required. The files are printed out onto ceramic-coated transparency film (such as Pictorico OHP Transparency Film or PermaJet Digital Transfer Film)⁸²⁴ using an Epson photo-quality ink-jet printer, like the R2880. The procedure provides internegatives, suitably matched in optical density at UVA wavelengths, for contact printing in any of the 'alternative' photographic processes. This digital negative workflow differs significantly from the customary practices in several respects:

- For calibration, 100-step-tablet negatives having intervals of 1% relative opacity, are inkjet-printed onto the film, identical in all their print parameters and materials with the actual negatives to be output. All the colours of the printer's ink-set are used, blended in a smooth greyscale.
- The Standard Printing Exposure (SPE) is found by printing these 100-step-tablet negatives in the process of choice with the standard printing setup, so that the clear filmbase (relative opacity of 0%) produces 'nearly' the maximum print density (D_{\max}) that the process is capable of, while some tonal separation is still visible in the deepest shadows (0–10%).
- The correct ink density range (at UVA wavelengths) for the negative to match the exposure scale of the chosen process is found by adjusting the printer driver settings: trial 100-step-tablet negatives are output and test-printed at the SPE, until the 99% relative opacity step in the negative prints as 'just white' background of the paper used for the process.
- Having established the 'black and white' end-points for the process, when making the negatives appropriate for analogue printing, the image levels are redistributed in Photoshop to ensure that mid-grey tones also print correctly. This is achieved simply by using the gamma slider in the Levels window, which applies a suitable 'generic curve' automatically; making the laborious derivation of a 'personalised' curve generally unnecessary.

IV.2 Calibration of equipment and materials

The optical density range of the ink laid down on the film depends on:

- the particular make and model of printer
- the particular ink set being used
- the choice of settings in the printer driver software
- the film substrate used to receive the negative image

If any of these are changed, it will be necessary to re-calibrate.

Calibration Procedure

1) Output the digital file for the 100-step-tablet to your printer.

Load the printer with the identical film that you will use for all your negatives. As a starting point, the ink density range may be approximately provided by the printer's 'premium photo-quality' media settings for glossy or semi-glossy paper, preferably an 'Advanced Black & White' setting if one is provided.

Use 'matt black' ink rather than 'photo black' if there is a choice.

The software for driving modern printers now usually includes a means of adjusting the maximum ink density; this control may be buried rather deeply in the options. Record its setting before outputting the 100-step-tablet files.

Let the test negative dry and cure overnight before use, as inks have been observed to change density with time.

2) Assemble the standard print-making setup for your chosen process.

Take care that the light source, distance, and other conditions of printing and wet-processing are maintained constant throughout.

3) Use your 100-step-tablet negative to make trial contact exposures.

Increase the exposure if necessary, until you have a test print that is perceptibly overexposed.

[N.B. 'Overexposure' here is judged by the analogue photographer's negative-working criterion of shadow tones beginning to 'block up' and become indistinguishable – it is NOT judged by the digital photographer's positive-working criterion of high values being 'blown out'.]

Call the exposure for this test print, E. If you are making timed exposures to a constant light source, E is simply the duration in minutes or seconds. If you employ an exposure system with a light integrator, E will be measured in the instrument's arbitrary 'exposure units'.

4) Examine the test print carefully when it is dry.

The lowest part will appear dense and 'blocked up' with no resolution of the sequential steps. Compare each step with the lighter one immediately *above* it – *i.e.* the one resulting from 10% less transmittance in the negative (=10% more opacity, corresponding to a density difference of ~0.05, or 1/6th of a 'stop'). Try to locate the first step, starting from the bottom, that is just perceptibly resolved in tone from the one above it; this lower step tells you the transmittance in this negative needed to produce your *effective* maximum print density. Call this transmittance P%.

5) Calculate your Standard Printing Exposure (SPE).

Take P% of E, the exposure for the test print made in 3):

$$\text{SPE} = E \times P/100$$

The SPE should apply approximately for all prints made in the chosen process, with your digital negatives, provided that the light-source and other printing and processing conditions are kept the same. Note that the SPE is *not* sharply-defined, but can be varied slightly, because the *effective* maximum

print density depends on how far up the shoulder of the characteristic curve of the chosen printing process it is placed. However, the higher the effective maximum density is placed, the greater proportion of the 256 image levels will need to be allocated to increasing separation in the shadow tones, so there will be fewer left for the lighter tones of the image, which compresses the contrast. Furthermore, if you seek to produce a 'maximum black' by extending the SPE excessively, the printer inks may not have sufficient UVA blocking opacity to produce a 'paper base white' at all.

6) Make a contact test print of the 100-step-tablet negative at the SPE.

Inspect the test print carefully, when fully dry, to find the step that appears 'just white' – *i.e.* the first one that has no upper boundary and which precedes the step with the first perceptible print tone.

7) If *no* steps print white, adjust the printer driver settings to lay down *more* ink when making the negative.

If several steps print white, adjust for *less* ink in the negative.

8) Return to Step 1) and make a new 100-step-tablet negative.

Use the new settings, and re-test it through Steps 2) to 7). The ideal aim is to get 'just white' for the *first* step of the tablet – that having 1% transmittance or 99% opacity – but it should be satisfactory to get within 2 or 3 steps of this. Experiment carefully with your printer driver settings: change the **maximum optical density** of the ink (a control usually found in the "colour management" window) and note its value when you make each new test negative. Print each one in your process with the same SPE until you come close to the ideal highlight tones.

IV.3 Fine-tuning negative opacities

This is only necessary in case your printer driver controls do not allow you to get the first white step close to 1% transmittance or 99% opacity. If it is still significantly different from this ideal value, then it will be necessary to reset the maximum opacity of the negative file to a value equal to the opacity observed for the first white step, before you output it on transfer film, so that the negative will print the white level correctly. The Layer Opacity Slider in the layers palette provides a convenient means of making this fine adjustment. All the other opacity values will then be scaled proportionally.

Setting the Layer Opacity to less than 100% makes the tonal separation a bit coarser in principle, because the tonal scale of the image will be resolved across fewer than the full 256 levels. If the printer driver settings result in a white value close to 100%, it's unlikely the eye will notice this, so this adjustment in the following Workflow should be no more than 'fine-tuning'.

IV.4 Tonal correction curves by the 'gamma' control

There usually *is* a need to redistribute the levels of a digital image file before it can provide a useful negative. If this is not done, a print made with the SPE will usually appear too dark in overall tonality, even though the black and white

IV.5 Workflow for digital negatives in Photoshop CS

Summary of the sequence of 'Things that may need to be done'

Phase I: Acquisition and digitization of image

- 1) Turn off Colour Management in Photoshop
- 2) Open Image File – if already available, or –
- 3) Scan Source – if necessary – and Save

Phase II: Preparation of positive image file

- 4) Preliminary Image Adjustments – if needed
- 5) Crop & Re-size Image
- 6) Monochromatize – if an RGB colour image
- 7) Burn & Dodge – if desired (a crude tool)
- 8) Set Black & White Levels
- 9) Adjust Local Contrast – in areas where needed
- 10) Retouch Flaws – where necessary
- 11) Save 'Perfected' Positive Image File

Phase III: Preparation of negative image file

- 12) Apply Tone Correction Curve to Positive by resetting Gamma
- 13) Reverse Handedness – if image reads correctly on screen
- 14) Invert Tonality from Positive to Negative
- 15) Sharpen Image with Unsharp Mask
- 16) Mask Print Border – if desired (expensive in ink)
- 17) Flatten Layers & Save 'Adjusted' Negative Image File

Phase IV: Printing the negative image onto film

- 18) Fine-tune Negative Opacity to Match Exposure Scale – if needed
- 19) Connect Printer. Load Film & Check Inks
- 20) Select Printer & Page Setup
- 21) Reduce Image File to 8 bits per channel if necessary
- 22) Set Printer Driver & Maximum Ink Density & Output the Negative
- 23) Number the Negative & allow ink to cure

Workflow for Making Digital Negatives in Photoshop CS

Phase I: Acquisition and digitization of image

Key	Menu or Tool	Procedure
Keys are Shortcuts to Tools and Menus: my F6, F7, F8 are re-defined: Edit>Keyboard Shortcuts		

1) Turn Off Colour Management in Photoshop

⌘↑K	Photoshop>Colour Settings> RGB: CMYK: Gray: Spot: Colour Management Policies:	In order to turn Colour Management OFF:- 'Monitor RGB - iMac' 'Euroscale Coated v2' or other suitable choice 'Gray Gamma 1.8' '0% Dot Gain' or as low as possible All OFF
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2) Open Image File - if already available

⌘O	File>Browse...>Open> If colour profiles mismatch:	Acquire raw image, preferably 16 bit/channel Negative or positive, preferably RGB Discard any embedded colour profile
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3) Scan Source - if necessary

File>Import>Epson Scanner Settings: Document Type: Film Type: Image Type: Scanning Quality: Resolution for 360 ppi negs: (Use higher if heavy crop)	Use Epson Scan Software in Professional Mode Save the following settings: 'Film (with Film Holder)' if a negative or slide 'Positive Film' '48-bit Color' Best Final Format: A5 A4 A3 Source Format: 10x8 in. 300 425 600 ppi 5x4 in. 600 900 1250 9x6 cm 900 1300 1850 6x6 cm 1300 1850 2700 35 mm 2100 3050 4350
Check Document Size:	10x8 in. 9.69x7.68 in. 246x195mm 5x4 in. 4.72x3.70 in. 120x94 mm 9x6 cm 3.25x2.20 in. 82x56 mm 6x6 cm 2.20x2.20 in. 56x56 mm 35 mm 1.417x0.945in. 36x24 mm
Target Size:	'Original'; Trimming: Off
Click Zoom button in Preview panel	for enlarged preview image of 6x9 etc
Set marquee	cropping as little as possible
Click Histogram button	to open histogram adjustment window
Check Output Levels	full range 0 to 255
Set Input Levels B&W sliders	on histogram; RGB channels; beware clipping
Click & Hold Show Output button	to see if there's any clipping bars at ends
Tone Adjustment	none: linear, centre slider gamma = 1.00
Auto Adjustments	none: turn off any
Densitometer	is useful to check B&W levels before scan
Click Close button	in histogram window
Click Scan button	to scan image and import into Photoshop
⌘↑S	File>Save As>'Raw Scans' Save scan as .tif file in folder 'Raw Scans' no compression

Phase II: Preparation of positive image file

4) Preliminary Image Adjustments – if needed

	Double Click 'Background' layer	to select it in Layers palette
	Click OK button in New Layer window	Converts Background to Layer 0 for adjusting
	<u><i>IF not suitably oriented:-</i></u>	
	Image>Rotate Canvas>...	to rotate image for normal viewing
	<u><i>IF a negative:-</i></u>	
⌘I	Image>Adjustments>Invert	to invert tonality to positive for easy viewing
⌘0	(zero) View>Fit on Screen	Gives optimum image window size
	<u><i>OR:-</i></u>	
Z	Select 'Zoom' tool	Click 'Fit on Screen' button

5) Crop & Re-size Image

	Image>Image Size...	Check re-sizing parameters correctly selected
	Tick boxes for	Scale Styles; Constrain Props; Resample: Bicubic
C	Select 'Crop' Tool	to frame and re-size the image:-
	Click Tool preset picker bar top left (allowing margin of ~0.15")	Select tool to re-size image at 360 ppi
		A5: 8.0 x 5.6 in 203x142mm 2880x2016px
		A4: 11.4 x 8.0 in 290x203mm 4104x2880px
		A3: 16.3 x 11.4in 414x290mm 5868x4104px
⌘R	View>Rulers	to show rulers, if desired
⇧	Shift Lock	to replace crop icon cursor with crosshairs
⌘⇧;	View>Snap	to switch 'snap to edge' on/off as desired
	Click & Drag within image	to generate a marquee defining image
⌘'	View>Show>Grid	to generate grid – if useful for placement
↔	Keys	move whole marquee finely: it rotates about Registration point – can be dragged to re-align
	<u><i>IF desired to correct perspective:-</i></u>	
	Tick perspective box in toolbar	to transform marquee:-
	Click & Drag corners of marquee	onto a would-be rectangle for the image
	Pull edge centres of marquee	to resize – keeping corners within frame (only possible if crop undimensioned)
✓	Click ✓ button	to execute Crop
	<u><i>OR:-</i></u>	
∅	Click ∅ button	to cancel and re-set

6) Monochromatize – if an RGB colour image

F8*	Image>Adjustments>Channel Mixer	opens window to convert to monochrome
	Click Load... button	for preset channels file
	Select 'mono.cha' file	saved file from Documents:
	Click Load	L = 30%R + 59%G + 11%B (visual response)
	Tick Monochrome box	Output Channel: Gray
	Click OK button	to apply channel mix and close window
	<u><i>OR if desired to set channels manually:-</i></u>	
⇕	Click each RGB channel	Study them for noise, or use as filter, then:-
	Arrow Keys to set channels	as preferred; total must sum to 100%
	Click OK button	to apply channel mix and close window
	Image>Mode>Grayscale	to revert image to grayscale (for smaller files)

7) Burn & Dodge – if desired (a crude tool)

<p>O Choose 'Burn' or 'Dodge' Tool Tool Options Bar>Brush Preset: Tool Options Bar>Range: Tool Options Bar>Exposure: Click & paint with tool <u>IF correction needed:-</u> Edit>undo</p>	<p>as required – alt click switches between them Brush Diam: 100–1000 pixels; Hardness: 0 Select from: Shadows, Midtones, Highlights Exposure slider: Try ca. 10–20% for intensity to burn or dodge areas of image. Can repeat or step back in History Palette and delete</p>
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8) Set Black & White Levels

<p>⌘L Image>Adjustments>Levels Alt Click B&W level sliders Click OK button</p>	<p>opens Histogram window: Set B&W levels: to view effect on image areas for Dmax & Dmin points. Keep <u>all</u> image levels: don't clip to execute Levels adjustments – or Cancel</p>
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9) Adjust Local Contrast – in areas where needed

<p>⌘alt0 View>Zoom In or Zoom Out <u>EITHER use 'Magnetic Lasso' Tool:-</u> L Choose 'Magnetic Lasso' Tool Click cursor on edge to select start [] Keys change Width in use Click to get marquee <u>OR use 'Magic Wand' Tool:-</u> W Choose 'Magic Wand' Tool Select>Grow ⌘L Image>Adjustments>Levels Re-set Slider for Centre Level Check Preview box to see effect Click OK button ⌘D <i>OR ESC</i></p>	<p>Magnify area, and select it:- Feather: 3–5 px; Antialias: off; Width: 10 px Edge Contrast: 10–20%; Frequency: 100 Move mouse slowly round area to be selected Can back-delete anchors; Click to set anchor Use wider for smooth edges when returned to the starting point Contiguous; ±Tolerance = range of levels Increases range Accesses Histogram window: Re-set gamma <1.00 to increase contrast Match densities using eyedropper if need be in Levels window to apply contrast – or Cancel to deselect Lasso, or Click within marquee</p>
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10) Retouch Flaws – where necessary

<p>⌘alt0 (zero) Click & Drag in scroll bars J Choose 'Healing Brush' Tool Click Brush menu Alt Click cursor on nearby area Click & paint ⌘0 (zero)</p>	<p>Zooms magnification to 100%. Seek defects:- Scan frames from top left, raster-like manner Blending mode: Replace; Source: Sampled Aligned; Brush Size: Off; Brush Spacing: 25% Brush Diameter: Try 12 pixels; Hardness: 0 to locate sampling of replacement density Repair defects with Healing Brush. Continue. to revert Zoom to normal when finished</p>
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11) Save 'Perfected' Positive Image

<p>⌘↑S Layer>Flatten Image File>Save As>'Positives360'</p>	<p>Flattens image to Background Layer (smaller) Save positive as .tif file in appropriate folder no compression; Mac byte order</p>
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Phase III: Preparation of negative image file

12) Apply Tone Correction Curve to Positive by Resetting Gamma

	Double Click Background Layer	to select it in Layers palette
	Click OK button in New Layer window	to convert 'Background Layer' to 'Layer 0'
	<u>EITHER use Centre-point slider:-</u>	
⌘L	Image>Adjustments>Levels	opens Levels window & Histogram
	Re-set Slider for Centre Level	Set Gamma to ca. 2.2 Record the value used
	Check Preview box to see effect	Positive image will look ~2 stops overexposed
	Click OK button	to apply curve & close Levels window - or Cancel
	<u>OR use a Stored Curve:-</u>	
⌘M	Image>Adjustments>Curves	opens adjustment curves control window:-
	Alt Click on grid	to improve coordinate grid to 10 divisions
	Load a selected .acv Curve	options stored for adjusting as desired by:
↓↑	Keys move any selected control point	'open' or 'close' highlights, midtones or shadows
	<u>OR Generate a Custom Curve: -</u>	by placing cursor on image area to modify:-
⌘M	Image>Adjustments>Curves	opens adjustment curves control window:-
	⌘Click the image area	to set a control point on the Curve
↓↑	Keys	darken or lighten this area, respectively
	⌘Click in another area	to set a point to be further adjusted likewise
	Click & Hold eyedropper in an area	to see where that area lies on the Curve
	ctrl-Tab moves selected point	through control points on Curve
	shift ctrl-Tab	moves through in reverse
	shift-Click	enables multiple points to be selected
	Click OK button	to apply Curve & close curves window - or Cancel

13) Reverse Handedness - if image reads correctly on screen

F7*	Edit>Transform>Flip horizontal	Laterally reverses picture to a mirror image
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14) Invert Tonality from Positive to Negative

⌘I	Image>Adjustments>Invert	Inverts image tonality to negative scale
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15) Sharpen Image with Unsharp Mask

F6*	Filter>Sharpen>Unsharp Mask	Amount: 100-250% usually 200%
		Radius: 0.5-1.5 pixels usually 0.8 pixel
		Threshold: 2-4 levels usually 3 (skin ~6)
	Tick Preview box	to see effect of USM when image clicked
	Click OK button	in USM window to apply USM - or Cancel

16) Mask Print Border - if desired (expensive in ink)

	Image>Canvas Size...	8.0x5.6 in. A5: 8.28x5.85 in. 210x149 mm
		11.4x8.0 in. A4: 11.70x8.28 in. 297x210 mm
		16.3x11.4in A3: 16.65x11.7 in. 421x297 mm
W	Choose 'Magic Wand' Tool	Antialiased; Contiguous; Tolerance 0
	Click with Wand in border area	to select border area to be masked
↑F5	Edit>Fill...	Colour: Black; Blending Mode: Normal
⌘D		to deselect border mask

17) Flatten Layers & Save 'Adjusted' Negative Image

⌘↑S	Layer>Flatten Image	Flattens image to Background Layer (smaller)
	File>Save As>'Diginegs'	Save negative as Tiff file in folder 'Diginegs'
	Click OK button	Tiff Options: No compression; Mac byte order

Phase IV: Printing negative image onto film

18) Fine-tune Negative Opacity to Match Exposure Scale – if needed

<p>If White ~99% Opacity skip this whole box:</p> <p>Double Click Background Layer</p> <p>Click OK button in New Layer window</p> <p>Click Image Layer Opacity button</p> <p>Adjust Image Layer Opacity slider</p> <p>Record the step% value used</p> <p>Click Image Layer Opacity button</p> <p>Layer>Flatten Image</p>	<p>ink density will be adjusted in printer settings 22)</p> <p>to select it in Layers palette</p> <p>to convert 'Background Layer' to 'Layer 0'</p> <p>to reveal Opacity Slider in Layers palette</p> <p>to a value matching process to be used:</p> <p>step % prints just white when 0 % prints near Dmax</p> <p>See: calibration of equipment & materials</p> <p>to close the Opacity Slider</p> <p>Flattens image to Background Layer</p>
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19) Connect Printer, Load Film & Check Inks

<p>Connect Printer & Switch ON</p> <p>Launch Printer Utility</p> <p>Click Status Monitor</p> <p>Choose Nozzle check</p> <p>Close Printer Utility window</p>	<p>Load Printer with one sheet digital transfer film</p> <p>Ensure correct Printer selected from List</p> <p>to check ink levels & recharge if needbe</p> <p>if printer long-dormant: head clean if needbe</p>
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20) Select Printer & Page Setup

<p>⌘↑P File>Page Setup...</p> <p>Click OK button</p> <p>Click in Doc: edge area</p> <p>Alt Click in edge area</p>	<p>Format for selected printer & paper size & Aspect</p> <p>in Page Setup window</p> <p>to see fit of image on page</p> <p>to see size of image, resolution, etc.</p>
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21) Reduce Image File to 8 Bits per Channel if necessary

Image>Mode>8 bits/channel	to prepare for sending to printer – if 8 bit
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22) Set Printer Driver & Maximum Ink Density & Output the Negative

<p>⌘altP File>Print with Preview...</p> <p>Colour Management:</p> <p>Click Print... button</p> <p>Printer:</p> <p>Presets:</p> <p>Print Settings>Media Type:</p> <p>Colour:</p> <p>Advanced Mode:</p> <p>Colour Management:</p> <p>Colour Controls:</p> <p>Extensions:</p> <p>Paper Configuration:</p> <p>Click Print button</p>	<p>Check page settings:- Check centred image Document; Profile: Same as Source</p> <p>to access Print Settings window:-</p> <p>Check printer choice correct</p> <p>Use tested & saved Printer Driver settings file:</p> <p>Appropriate paper choice (photo or matte)</p> <p>Colour ON</p> <p>Premium Photo Quality: highest resolution dpi</p> <p>High speed OFF; Mirror image OFF</p> <p>Mode: Epson Standard sRGB</p> <p>All sliders centred; gamma = 2.2</p> <p>Advanced B&W mode: Neutral & 'Normal' tone</p> <p>Adjust maximum ink density to give White~99%</p> <p>Normal paper (not thick)</p> <p>Colour density & head drying time – defaults</p> <p>to print out the negative on transparency film</p> <p>Don't 'Save Changes' on closing file</p>
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23) Number the Negative & Allow Ink to Cure

Number the negative indelibly	Allow negative to dry in dust-free environment for at least 12 hours before use. Do not stack.
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IV.6 Short version of the workflow

The previous detailed workflow was designed to cope with most eventualities, but it has necessarily become so lengthy that it is “hard to see the wood for the trees”. If we are working with preformatted and ‘perfected’ positive images, the following are the only essential steps needed to prepare a tonally-corrected and density-adjusted negative.

Numbers refer to the original ‘Things that may need to be done’ boxes.

- 1) **⌘↑K** Photoshop>Colour Settings> Colour management **OFF**
- 4) **Double Click ‘Background’** in Layers palette
Click OK New Layer 0
- 6) **F8*** Image>Adjustments>Channel Mixer
Load ‘mono.cha’ file: L = 30%R + 59%G + 11%B
 Image>Mode>Greyscale
- 8) **⌘L** Image>Adjustments>Levels
Alt Click Sliders & Set B&W levels
- 12) **Set Middle Slider to Gamma \approx 1.8 – 2.4** for desired contrast
- 13) **F7*** Edit>Transform>Flip horizontal
- 14) **⌘I** Image>Adjustments>Invert
- 15) **F6*** Filter>Sharpen>Unsharp Mask
- 18) **IF** maximum ink density *cannot* give White for the 99% Opacity step in (22):
 Adjust Image Layer Opacity to the % Opacity of the first 'white step'
 Layer>Flatten Image
- 19) **Launch Printer Utility:** Ensure Printer connected, loaded, and switched on
Click Status Monitor to check ink levels etc
- 20) **⌘↑P** File>Page Setup... Format for Printer, Page, Paper size & aspect ratio
- 22) **⌘altP** File>Print with Preview...
Click Print... Print Settings: Advanced B&W mode
 Neutral & ‘Normal’ tone
Adjust Maximum Ink Density to the value that gives ~99% Opacity in the negative printing as the 'white step'.
Click Print

* reassigned function keys

APPENDIX V

Alphabetical List of Relevant Chemicals

Description of Chemicals

The history of chemical nomenclature shows that substance names in the past were frequently idiosyncratic and irrational. The imprecision of using shortened 'popular' names for certain common chemicals has finally been resolved in recent years, but at a price. The recommendations of the International Union of Pure and Applied Chemistry (IUPAC) are necessarily intricate and – in spite of the name of that body – by no means universal in their acceptance and use. Chemical nomenclature confronts the lay person with a minefield to negotiate – even professional chemists find it tiresome, and most prefer to use the more concise and specific shorthand of chemical formulae. A unique and universal reference for most chemicals is provided by the Registry Number of the Chemical Abstracts Service, CASRN, and is widely used in chemical catalogues. It is denoted in the lists below by CAS. If you are in doubt about the identity of a chemical from its name, then cross-check this number, but note that the same chemical in different states of purity may be designated by different numbers.

For the benefit of the chemically numerate reader, the molecular formula and relative molecular mass (denoted here by RMM, also known as the formula weight FW) are given in the lists below as a convenient reference for making your own calculations.

Regarding a suitable specification of purity for the chemicals, the grade known as GPR (standing for General Purpose Reagent) usually guarantees a purity in the order of 97–99%, and is adequate for our purposes. In the USA the term SLR is sometimes used (Standard Laboratory Reagent). Higher degrees of purity are, of course, acceptable, but will usually incur greater expense.

In the lists below, the corresponding catalogue numbers are quoted for the following major suppliers of fine chemicals, where appropriate:

Aldrich–Sigma Chemical Company Ltd
Alfa Aesar (A Johnson Matthey Company)
Bryant (A Spectrum Chemical Company)
Fluka (Riedel de Haën)
Merck (BDH)

The hazards associated with the chemicals listed are only briefly summarised below: the information has been abstracted from the published Materials Safety Data Sheets, which should always be consulted for more details. The hazards fall into three main categories:

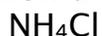
Health (toxicity, or other threat as carcinogen or teratogen, when ingested or inhaled, or absorbed through the skin, and the risk due to direct contact causing corrosive damage to eyes, skin, or mucosa)

Flammability (tendency to combustion)

Reactivity (tendency to violent reactions with common materials: air, water, etc.). The two latter categories hardly apply to any of the chemicals used here.

Alphabetical List of Relevant Chemicals

Ammonium chloride



RMM = 53.49

CAS 12125-02-9

Aldrich #21,333-0 ; Alfa #12361, or #40193; Bryant #A335; Fluka #09700 or #09702 or #11212; Merck #159041 or #101141

Also known as: sal ammoniac.

Hazards: Harmful if swallowed. Skin, eye, and respiratory irritant.

Ammonium iron(III) oxalate (trihydrate)



RMM = 428.07

CAS 13268-42-3; 14221-47-7

Aldrich #23007-3; Alfa #42112; Bryant #F335 (Spectrum #F1002); Fluka #12302; Citychemical #F393

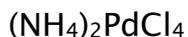
Also known as: iron ammonium oxalate; ammonium ferric oxalate; ferric ammonium oxalate; ammonium trisoxalatoferrate(III) trihydrate.

Hazards: Harmful if swallowed, inhaled or absorbed through the skin.

Corrosive – causes burns. Very destructive of mucous membranes.

Toxicology not fully investigated.

Ammonium tetrachloropalladate(II)



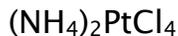
RMM = 284.29

CAS 13820-40-1

Aldrich #20,585-0; Alfa #11882, or #10824;

Hazards: Harmful by ingestion. Irritating to eyes. Possible risk of irreversible effects. Possible carcinogen.

Ammonium tetrachloroplatinate(II)



RMM = 372.98

CAS 13820-41-2

Aldrich #20,610-5; Alfa #11046

Hazards: Toxic by ingestion. Irritating to eyes. Can cause dermatitis and skin sensitization. Exposure can cause asthma, shortness of breath and cyanosis. Allergenic. Evidence of mutagenic effects.

Calcium chloride (anhydrous)



RMM = 110.99

CAS 10043-52-4

Aldrich #22,231-3 ; Alfa #12316, or #33327; Bryant ; Fluka #21074 or #21079; Merck #102391 or #102379

Hazards: Harmful if swallowed. Eye, skin, and respiratory irritant. Ingestion of large amounts can lead to hypercalcaemia, dehydration and renal damage.

Calcium nitrate (tetrahydrate)

$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$

RMM = 236.15

CAS 13477-34-4

Aldrich #23,712-4; Alfa #12364;

Hazards: Harmful if swallowed. Eye, skin, and respiratory irritant. Ingestion of large amounts can lead to hypercalcaemia, dehydration and renal damage.

Citric acid

$\text{C}(\text{OH})\text{COOH} \cdot (\text{CH}_2\text{COOH})_2$

RMM = 192.12

CAS 77-92-9

Aldrich #25,127-5 or #C8,315-5; Alfa #31185; Bryant #C350; Fluka #27488 or #27109 or #03878; Merck #818707 or #100247

Also known as: 2-hydroxypropane-1,2,3-tricarboxylic acid; 2-hydroxypropane-1,2,3-trioic acid.

This substance is also obtainable as a monohydrate CAS 5949-29-1. RMM = 210.14. Either form will do.

Hazards: Severe eye irritant. Skin and respiratory irritant. Prolonged or repeated exposure may cause allergic reaction in some individuals.

1,2-Diaminoethanetetraethanoic acid, disodium salt (dihydrate)

$\text{C}_2\text{H}_4(\text{N}(\text{CH}_2\text{COOH})(\text{CH}_2\text{COONa}))_2 \cdot 2\text{H}_2\text{O}$

RMM = 372.24

CAS 6381-92-6

Aldrich #25,235-2; Alfa #33312; Fluka #27285 or #03685 or #27270

Also known as: ethylenediamine tetraacetic acid, disodium salt; 1,2-diaminoethanetetraacetic acid, disodium salt; ethylenedinitrilotetraacetic acid, disodium salt; disodium edetate; sequestrene Na_2 ; disodium EDTA; Na_2EDTA .

Hazards: Harmful if swallowed; may be harmful if inhaled or through skin contact. Eye, respiratory tract and skin irritant.

1,2-Diaminoethanetetraethanoic acid, tetrasodium salt (dihydrate)

$\text{C}_2\text{H}_4(\text{N}(\text{CH}_2\text{COONa})_2)_2 \cdot 2\text{H}_2\text{O}$

RMM = 416.21

CAS 10378-23-1

Aldrich #E2,629-0; Bryant #E315; Fluka #03695; Merck #108436

Also known as: ethylenediamine tetraacetic acid, tetrasodium salt; 1,2-diaminoethanetetraacetic acid, tetrasodium salt; ethylenedinitrilotetraacetic acid, tetrasodium salt; tetrasodium edetate; tetrasodium EDTA; Na_4EDTA .

This substance is also obtainable as a tetrahydrate, CAS 13235-36-4. Either form will do.

Hazards: Eye, skin and respiratory irritant.

Dimethyl sulphoxide

$(\text{CH}_3)_2\text{SO}$

N.B. Freezing point 18 °C (64 °F) (99% pure).

RMM = 78.13

CAS 67-68-5

Aldrich #M8,180-2; Alfa #16897; Fluka #41650 or #60153; Merck #802912 or #102952

Hazards: Skin, eye and respiratory system irritant. Readily absorbed through skin. Toxic if swallowed. Experimental tumorigen and teratogen. Reacts violently with a number of materials.

Ferric Oxalate See Iron(III) oxalate (hexahydrate)

Hydrochloric acid 36.5%

HCl

RMM = 36.46

CAS 7647-01-0

Aldrich #25,814-8; Alfa #

Hazards: Causes severe burns to eyes and skin. If ingested causes severe internal irritation and damage. Extremely irritating, harmful vapour.

Hydrogen peroxide 27% w/w

H_2O_2

RMM = 34.01

CAS 7722-84-1

Aldrich #21,676-3; Alfa #

Hazards: Causes severe burns to skin and eyes. Extremely irritating to respiratory system. If ingested, sudden evolution of oxygen may cause injury by acute distension of the stomach, and may cause nausea, vomiting and internal bleeding.

Hydrogen tetrachloroaurate(III) (trihydrate)

$\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$

RMM = 393.83

CAS 27988-77-8 (very high purity)

16961-25-4 (high purity)

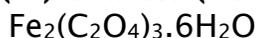
16903-35-8 (acceptable purity)

Aldrich #24,459-7 or #25,416-9; Alfa #36400 or #12325; Bryant #G335; Fluka #50780 or #50790 or #12502 or #12503 or #50800; Merck #101582

Also known as: chloroauric acid; hydrochloroauric acid; auric chloride hydrochloride; gold(III) chloride hydrate, or, (in the earlier literature, which was ambiguous and inaccurate) as 'gold chloride'.

Hazards: Corrosive – causes burns. Extremely destructive of mucous membranes. Harmful by ingestion or inhalation. May cause allergic skin reaction.

Iron(III) oxalate (hexahydrate)



RMM = 483.84

CAS 19469-07-9

Aldrich #38,144-6; Alfa #31116

Also known as: ferric oxalate

Hazards: Harmful by ingestion and skin contact. Irritating to skin and eyes.

Lead(II) acetate (trihydrate)



RMM = 379.33

CAS 6080-56-4

Aldrich #21,590-2; Alfa #14242

Hazards: Harmful by ingestion and if inhaled as dust. Major hazard is due to cumulative effects of lead. Symptoms include digestive disturbances, pallor, anaemia, blue line on gums. Irritating to eyes. Carcinogenic.

Lead(II) nitrate



RMM = 331.20

CAS 10099-74-8

Aldrich #22,862-1; Alfa #14243

Hazards: Harmful by ingestion and if inhaled as dust, causing severe internal injury. Major hazard is due to cumulative effects of lead. Symptoms include digestive disturbances, pallor, anaemia, blue line on gums. Irritating to eyes.

Mercury(II) chloride



RMM = 271.50

CAS 7487-94-7

Aldrich #21,546-5; Alfa #12274

Hazards: Very toxic by ingestion, inhalation and skin contact, causing nausea, vomiting, abdominal pain, diarrhoea, and headache. Continued exposure may cause severe nervous disturbance, loosening of teeth, and heavy salivation. Danger of cumulative effects. Irritating to eyes and skin.

Nitric acid 65-70%



RMM = 63.01

CAS 7697-37-2

Aldrich #25,811-3; Alfa #33260

Hazards: Causes severe burns to eyes and skin. If ingested causes severe internal irritation and damage. Irritating harmful vapour.

Oxalic acid (dihydrate)

$(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$

RMM = 126.07

CAS 6153-56-6

Aldrich #24,753-7 or #O-875-5; Alfa #33262; Bryant #O226; Fluka #75702 or #27725; Merck #818242 or #100495

Hazards: Harmful if swallowed, inhaled or absorbed through skin. Corrosive – causes burns. Very destructive of mucous membranes. May cause congenital malformation in the foetus: possible teratogen.

Palladium(II) chloride

PdCl_2

RMM = 177.31

CAS 7647-10-1

Aldrich #20,588-5; Alfa #11034

Hazards: Harmful by ingestion and if inhaled as dust. Irritating to eyes. Possible risk of irreversible effects. Possible carcinogen.

Potassium aluminium sulphate (dodecahydrate)

$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

RMM = 474.38

CAS 7784-24-9

Aldrich #23,708-6; Alfa #36288

Also known as: Potash alum, aluminium potassium sulphate.

Hazards: Irritating to eyes.

Potassium chlorate

KClO_3

RMM = 122.55

CAS 3811-04-9

Aldrich #22,486-3; Alfa #36494

Hazards: Harmful by ingestion and if inhaled as dust, causing nausea, vomiting and abdominal pain. May cause kidney damage. Irritating to skin and eyes. Explosive in contact with combustible material and reducing substances.

Potassium dichromate

$\text{K}_2\text{Cr}_2\text{O}_7$

RMM = 294.19

CAS 7778-50-9

Aldrich #20,924-4; Alfa #13450

Hazards: Harmful by inhalation, ingestion and skin contact. Corrosive to skin and eyes. Frequent exposure to dust can cause ulceration, liver and

kidney disease and cancer. Inhalation of dust can cause nasal ulcers. Carcinogen. May ignite combustible material.

Potassium dihydrogen phosphate



RMM = 136.09

CAS 7778-77-0

Aldrich #22,130-9; Alfa #11594

Hazards: May irritate eyes and respiratory system if inhaled as dust.

Ingestion of large amounts of phosphate can cause serious disturbances in calcium metabolism.

Potassium oxalate (monohydrate)



RMM = 184.24

CAS 6487-48-5

Aldrich #22,342-5; Alfa #13452

Hazards: Harmful by ingestion and inhalation. Irritating to skin and eyes. If swallowed causes severe internal pain, followed by collapse.

Potassium tetrachloroplatinate(II)



RMM = 415.11

CAS 10025-99-7

Aldrich #20,607-5; Alfa #11048

Also known as: potassium chloroplatinite.

Hazards: Toxic by ingestion. Irritating to eyes. Can cause dermatitis and skin sensitization. Exposure can cause asthma, shortness of breath and cyanosis. Allergenic. Evidence of mutagenic effects.

Sodium carbonate (anhydrous)



RMM = 105.99

CAS 497-19-8

Aldrich #22,353-0; Alfa #11552; Bryant #S324; Fluka #71351 or #13418 or #71352 or #13419; Merck #159735 or #106393

Hazards: Eye and respiratory irritant.

Sodium chloride



RMM = 58.44

CAS 7647-14-5

Aldrich #22,351-4; Alfa #12314; Bryant #S328; Fluka #13423 or #71381; Merck #106404 or #159302

Also known as: common salt, table salt.

Hazards: May cause skin, eye, or respiratory irritation.

Sodium citrate (dihydrate) $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$

RMM = 294.10

CAS 6132-04-3

Aldrich #85,578-2; Alfa #36439

Also known as: trisodium citrate*Hazards:* Ingestion of large amounts may cause diarrhoea, nausea. May irritate eyes and respiratory system if inhaled as dust.**Sodium dithionite** $\text{Na}_2\text{S}_2\text{O}_4$

RMM = 174.11

CAS 7775-14-6

Aldrich #15,795-3; Alfa #33381

Also known as: sodium hydrosulphite*Hazards:* Harmful by ingestion and if inhaled. Irritating to skin and eyes.**Sodium ferric oxalate (trihydrate)** $\text{Na}_3\text{Fe}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$

RMM = 442.93

CAS 555-34-0

Hazards: Harmful if swallowed, inhaled or absorbed through the skin. Very destructive of mucous membranes. Toxicology not fully investigated.**Sodium hydrogen carbonate** NaHCO_3

RMM = 84.01

CAS 144-55-8

Aldrich #23,652-7; Alfa #14707; Bryant #S316; Fluka #71360 or #13433;

Merck #106329

Also known as: sodium bicarbonate; bicarbonate of soda; baking soda.*Hazards:* May irritate eyes .**Sodium hydroxide** NaOH

RMM 40.00

CAS 1310-73-2

Aldrich #22,146-5; Alfa #13455; Bryant #S350; Fluka #71692 or #06213;

Merck #106482 or #159319

Also known as: caustic soda.*Hazards:* Very corrosive. Causes severe burns. May cause serious permanent eye damage. Very harmful by ingestion. Harmful by skin contact or inhalation of dust.**Sodium metabisulphite** $\text{Na}_2\text{S}_2\text{O}_5$

RMM = 190.10

CAS 7681-57-4

Aldrich #25,555-6 or #16,151-9; Alfa #33375 or #40115; Bryant #S342; Fluka #71930 or #13459; Merck #106528.

Also known as: sodium pyrosulphite, sodium disulphite.

Hazards: May act as an irritant or be harmful if swallowed. May act as an allergen in sensitive individuals.

Sodium sulphite

Na_2SO_3

RMM = 126.04

CAS 7757-83-7

Aldrich #23,932-1; Alfa #13454; Bryant #S360; Fluka #71991 or #13471 or #71990 or #13472; Merck #106657

Hazards: Possible mutagen. Harmful by inhalation, ingestion and skin contact. Eye, skin and respiratory irritant. Prolonged or repeated exposure may cause allergic reaction.

Sodium tetrachloroaurate(III) (dihydrate)

$\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$

RMM = 397.8

CAS 13874-02-7

Aldrich #29,817-4; Alfa #84000; Fluka #12537

Also known as: sodium chloroaurate, sodium gold chloride.

Hazards: Corrosive. Destructive of mucous membranes. May be harmful by ingestion or inhalation. May cause allergic skin reaction.

Sodium tetrachloropalladate(II) (trihydrate -approx.)

$\text{Na}_2\text{PdCl}_4 \cdot 3\text{H}_2\text{O}$

RMM = 294.19 (anhyd.)

CAS 13820-53-6

Aldrich #20,581-8; Alfa #11886

Hazards: Harmful by ingestion. Irritating to eyes. Possible risk of irreversible effects. Possible carcinogen.

Sulphuric acid ca. 98%

H_2SO_4

RMM = 98.08

CAS 7664-93-9

Aldrich #25,810-5; Alfa #33273

Hazards: Causes severe burns to eyes and skin. If ingested causes severe internal irritation and damage. Dilute acid irritates the eyes and skin and may cause burns and dermatitis.

Tween 20™

$\text{C}_{58}\text{H}_{114}\text{O}_{26}$

RMM = 1227.54

CAS 9005-64-5

Aldrich #27,434-8; Alfa #43309; Bryant #T355; Fluka #93773 or #63158;
Merck #822184 or #817072

Also known as: polyoxyethylene (20) sorbitan monolaurate; Polysorbate
20™.

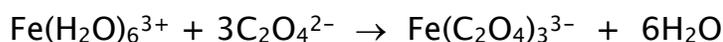
Hazards: eye irritant.

APPENDIX VI Chemical Preparations

VI.1 Ammonium ferric oxalate

If ammonium iron(III) oxalate is not readily available, a solution of it may be easily prepared by using the following procedure.

34 g of iron(III) nitrate nonahydrate, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, in a Pyrex vessel is gently heated to *ca.* 50 °C in a bath of hot water, until the pale purplish-brown crystals appear to ‘melt’ – actually they are dissolving entirely in their own water of crystallization – to give a deep red-brown solution. To this is added 35 g of finely powdered ammonium oxalate monohydrate, $(\text{COONH}_4)_2 \cdot \text{H}_2\text{O}$, with stirring at 50 °C (toxic: protect yourself with a mask against inhaling the dust) until all is dissolved to yield a clear emerald-green syrupy solution. The reaction is a simple displacement of bound water by the chelating oxalate ligand:



This solution can be used directly as a sensitizer without further purification: it must be diluted by adding *ca.* 14 cm³ of water, which should then give a total of 60 cm³ of a 1.4 molar solution of ammonium iron(III) oxalate. This solution will, of course, also contain a high concentration (8.4 M) of excess ammonium nitrate, NH_4NO_3 , which once coated onto paper tends to deliquesce, attracting water into the sensitized layer. It therefore acts as a humectant promoting the colours and contrast typical of the highly humidified papers, but does not otherwise seem to interfere in the process.

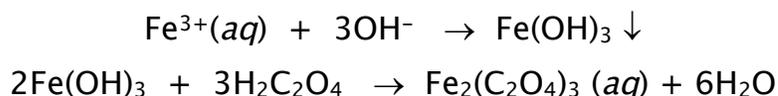
If it is desired to isolate the pure solid ammonium iron(III) oxalate, $(\text{NH}_4)_3\text{Fe}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$, the undiluted green syrup as prepared above should be set aside in the dark to cool and crystallise. The fine emerald-green crystals of ammonium iron(III) oxalate trihydrate are filtered off and washed with methanol, in which ammonium nitrate, the by-product, is quite soluble. The product may be recrystallised from a water-ethanol mixture, (recrystallization from water-methanol tends to give a complex with methanol incorporated in the lattice). The solid should be dried in normal air and stored in the dark, (drying over a desiccant such as anhydrous calcium chloride or silica gel will cause efflorescence and the loss of water of crystallization). The salt is very soluble, a saturated solution at 20 °C having a concentration of *ca.* 1.4 molar.

VI.2 Ferric oxalate

Because ferric oxalate is an ill-defined polymeric substance, the properties of the solutions and solids resulting from the methods of preparation described below will vary considerably. The polymeric solid salt is more difficult to isolate in a tractable form, which is amorphous, and has not, so far, been crystallised.

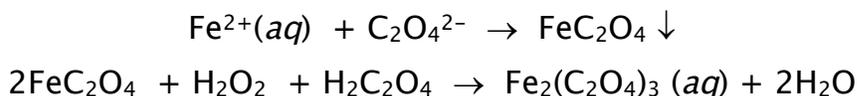
Solutions of iron(III) oxalate *ca.* 20–25% *w/v* may be prepared by several differing methods, which are reviewed by Dick Stevens in his first book on Kallitype.⁸²⁵ Although he lists seven variations, there are only four methods that differ essentially in their chemistry:

1) Precipitation of fresh iron(III) hydroxide by alkali from a solution of an iron(III) salt, followed by dissolving it in oxalic acid solution:⁸²⁶

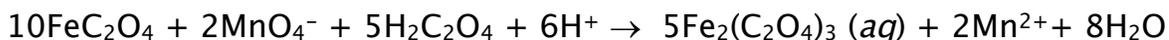


This method for making ferric oxalate solution has several variations, depending on the choice of iron(III) salt, as ferric chloride or ammonium ferric sulphate, and of the alkali, as sodium hydroxide, sodium carbonate, or ammonia; these alternatives were discussed by E.J. Wall in 1902.⁸²⁷ A basic procedure is given on the Bostick & Sullivan website.⁸²⁸ A slightly different version of this method, which is attributable to Pizzighelli and Hübl in 1882,⁸²⁹ is described in French by Jean-Claude Mougin,⁸³⁰ who also provides online an illustrated account in English of this method, and compares the printing performance of the different products.⁸³¹ Recently, Ian Leake has published an e-book describing Pizzighelli's method of preparing ferric oxalate solution.⁸³²

2) Precipitation of iron(II) oxalate by oxalic acid from a solution of an iron(II) salt, followed by its oxidation by hydrogen peroxide (or potassium permanganate) in the presence of excess oxalic acid:⁸³³

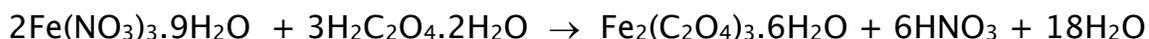


This method is recommended and recently described online by Eric Neilsen.⁸³⁴ It may be noted that pure iron(II) oxalate can be purchased at little expense. An alternative oxidant, manganate(VII), has been suggested but leaves a by-product of manganese(II) behind:



which is a less desirable method.

3) The reaction of solid iron(III) nitrate with solid oxalic acid:⁸³⁵



This method was perfected by Vicente-M. Vizcay Castro in 1999, and is said to produce a solid, in amorphous powder form, of high quality.⁸³⁶ A detailed description of the lengthy procedure has been placed online by Jeffrey D. Mathias.⁸³⁷

4) The double decomposition of barium oxalate with iron(III) sulphate.⁸³⁸



This method appears to have been little-used.

APPENDIX VII

Specifications of William Willis's British Patents

VII.1 N° 2011, June 5th, 1873

Improvements in Photo-chemical Printing.

This invention has for its object improvements in the chemical treatment of the surfaces of paper, wood and other suitable materials employed for receiving images from photographic negatives or from any other object that may be interposed between the light and such prepared paper or other surface. For this purpose according to my Invention I apply to surfaces of paper, wood, and other suitable materials (by either one or more coatings) solutions or coatings of simple or compound salts of platinum, iridium, or gold, or a mixture of such salts. After this has dried I sometimes apply another coating of a solution of a salt or salts of other metals. I then coat the material again, using a solution of ferric oxalate, or tartrate, or a combination of these salts with others, and again dry. I then expose the coated surface to light under a photographic negative or other suitable object until a faint brown image appears; after this I apply to the coated surface a solution of the neutral oxalate of potassium or other suitable oxalate, which speedily changes the brown tints to black ones. I then wash the surface thus treated for a short time in a dilute acid, and finally wash in water; but I sometimes immerse the surface in a solution of chloride of sodium, or hyposulphite of sodium, or other suitable salt before giving it a final wash in water.

The following are several examples of the operations and manner in which I employ some of the chemicals above referred to in carrying my Invention into practice.

First Method

I coat paper with a solution of the chloro-platinate of potassium containing 10 grains of the salt to 1 oz. of water. After drying the paper I coat it again with a solution of the nitrate of lead, 40 grains of the salt to 1 oz. of water, and dry it again. I then coat it a third time with a solution composed of ferric oxalate, 60 grains to 1 oz. of water, with as little oxalic acid as is sufficient to render the ferric oxalate soluble. I then dry the paper and expose it to light under a negative. On removing it from the negative I float it face downwards on a hot solution of potassic oxalate. I then wash it in a weak solution of oxalic acid, then in plain water, and finish by immersing it in a solution of hyposulphite of soda followed by a slight wash in plain water.

Second Method

In this method I proceed as in the first, but substitute an 8 grain solution of nitrate of silver for the nitrate of lead, and after removing the prints from the weak solution of oxalic acid I finish them by an immersion in either a strong solution of chloride of sodium, or in a weak solution of that salt, followed by a weak solution of ammonia, supplemented in both cases by a slight wash in plain water.

Third Method

I coat paper with a solution of platinic bromide, 12 grains to 1 oz. of water, and dry. I then coat it with a strong solution of ferric tartrate, and dry. I next expose this paper to light under a negative, and afterwards float it face downwards on a hot solution of potassic oxalate. I then immerse it in a weak solution of oxalic acid, and finish by washing it in plain water.

I occasionally vary the proceeding operations, or invert their order, or omit one or more of them.

I would remark that I do not intend to confine myself to the use of aqueous solutions of the chemicals herein-before referred to, as the salts may be dissolved and used in any suitable solvent.

I sometimes mix two or more of the salts used for coating the paper or other surface before application.

Having thus fully described the nature of my improvement, and the manner of carrying the same into practice, what I claim for the production (on suitable surfaces) of photographic pictures in platinum, iridium, and other metals is, the application of solutions of potassic, ammoniac, or other suitable oxalate to such surfaces after they have been exposed to light under a negative or other suitable object, and which surfaces have been coated previous to such insolation with ferric and with other salts substantially in the manner herein-before described.

VII.2 N° 2800, July 12th, 1878**An Improved Process of Photo-chemical Printing.**

This invention is based upon the process described in the Specification of my former Letters Patent, dated June 5th, A.D. 1873, N° 2011, which process consists in the production on suitable surfaces, such as paper, wood, silk, prepared canvas, and others, of photographic pictures in platinum, iridium, or other metal by the application of solutions of potassic or ammoniac oxalate to such surfaces after they have been exposed to light or insolated under or behind a negative or other object, and which surfaces have been coated previously to such insolation with ferric and other salts, one of which is a salt of the metal in which the picture is to be produced.

But although good results are produced by the process above set forth, I have discovered means whereby I obtain greatly superior results in photo-chemical printing and produce pictures or images characterized by great permanence, and am enabled to effect such printing in a more simple and certain manner, and with greater uniformity in the results than heretofore; and these improved means form the subject of my present invention.

The said Invention consists in an improved process of photo-chemical printing, whose essential feature is the addition of a salt of platinum, or of iridium, or of mercury to the solution of potassic or ammoniac oxalate used as described in the former Specification, and which improved process is as follows, that is to say :— The application to paper or other surfaces of a solution consisting of potassic or ammoniac oxalate mixed with a salt of platinum, of iridium, or of mercury after such paper or other surface has been exposed to light under or behind a negative or other object, and which paper or surface has previously to such exposure to light received a coating of or has been treated with ferric oxalate and with other salts, one of which is a salt of the metal in which the picture or image is to be produced on the said paper or other surface.

According to the said Invention I proceed as follows, that is to say :— If paper is used I coat the same with an aqueous solution which I term the coating solution, and which must contain as one of its ingredients a salt of the metal in which the picture or image is to be produced. For instance, when I desire to produce the picture in metallic platinum each fluid ounce of this solution will contain about 15 grains of potassic chloro-platinite, 70 grains of ferric oxalate (with enough oxalic acid to render this ferric oxalate freely soluble), and preferably two grains of plumbic chloride. I then dry the paper and expose it to light under or behind the negative or other object from which the picture or image is to be produced on the prepared paper for a sufficient time, which will usually be indicated by the image or picture becoming faintly visible. I then float the said paper with its face or coated surface downwards on or immerse it in an aqueous solution, preferably hot, which I term the developing solution, and whose use in the process constitutes the novel and essential feature of my Invention. Each fluid ounce of this developing solution contains 120 grains of potassic oxalate and 7 grains of potassic chloro-platinite, or other salt of the kind herein-after specified. This solution quickly deepens in color or blackens the picture or image produced on the coated paper by the action of light. I then

wash the paper in a weak solution of some acid (preferably oxalic acid), and finish by washing it in plain water.

The coating solution or solutions for treating the paper or other surface previous to its insolation or exposure to light constitutes no part of my Invention irrespective of the subsequent treatment of the coated surfaces by the developing solution ; and I may use other salts of platinum in this coating solution, or salts of other metals than those named above, such as salts of gold, iridium, or of palladium; but it is essential in all cases that ferric oxalate should form one of the ingredients or constituents of the coating or coatings applied to the said surfaces.

The following are examples of the manner in which I vary the composition of the said coating solution or solutions :—

I sometimes substitute 15 grains of iridium chloride for the potassic chloro-platinite used as above specified; or I substitute for the two grains of plumbic chloride 4 grains of mercuric chloride. In other cases I omit the plumbic chloride in the coating compound or solution.

Instead of effecting the coating of the paper or other surface with the aforesaid salts by using the same all in one solution, I may in some instances find it desirable to apply such salts in different successive solutions, and dry the paper, if necessary, between the successive coatings.

I do not confine myself to the use of potassic chloro-platinite as an addition to the aforesaid developing solution, that is to say the solution of potassic oxalate, which I apply to the insolated surfaces, but may use other salts of platinum or salts of iridium or mercury, such as platinic chloride, potassic chloro-platinate, or sodic, ammoniac, or baric chloro-platinite, iridic chloride, or mercuric chloride. But although these and other salts of the above named metals (namely, platinum, iridium, and mercury) when added to or mixed with the potassic oxalate will produce good results, I prefer to employ the potassic chloro-platinite for the purpose of my Invention as above set forth.

Nor do I intend to confine myself to the use of aqueous solutions of the chemicals herein-before referred to, as the salts may be dissolved and used with any suitable solvent.

Neither do I restrict myself to the exact proportions of the chemicals used in the above described process, as above stated, as these proportions may be varied within certain limits, according to the results desired to be obtained or other conditions.

In the final treatment of the paper or other material I do not confine myself to the use of acids, but may employ a solution of any other suitable substance capable of dissolving out the salts or chemicals which may be left in the paper.

Having thus fully described the said Invention, and the manner of performing the same, I wish it understood that I claim the improved process of photo-chemical printing, wherein I employ the aforesaid developing solution consisting of a salt of platinum, of iridium, or of mercury mixed with potassic or ammoniac oxalate, as for the purposes specified.

VII.3 N° 1117, March 15th, 1880**Improved Materials and Processes for Photo-chemical Printing.**

My present Invention is based partly upon the process of photo-chemical printing described in the Specification of my former Letters Patent, dated June 5th, A.D. 1873, N° 2011. By the said process the paper or other surface was coated with a solution of platinum, iridium, or gold, or a mixture of these salts, and sometimes other salts, and then with ferric oxalate or tartrate. In practicing the said process it was found necessary to use a salt of lead or of silver, and after exposure to light the said surface was treated with a solution of potassic or other suitable oxalate, but I have now discovered that I can dispense with the lead and silver salts, and by avoiding their use can obtain greatly superior results. By this improvement all danger of discolouration of the white portion of the prints arising from the use of metals other than iron and platinum is completely avoided. Moreover this improved process will be simpler than the said former process, and will obviate all liability to failure otherwise from improper exposure or carelessness.

My present Invention comprises paper or other material with its surface prepared and rendered sensitive for photographic purposes by the application of a coating solution containing platinous and ferric salts in such proportions or quantities as are hereinafter specified. The term platinous is used in this Specification in its chemical sense to distinguish the salts designated by it from those known as platinic salts.

The said Invention also comprises an improved process consisting in first preparing the paper or other surface by the use of the coating containing platinous and ferric salts as hereinafter specified, then exposing it to light under or behind a negative, and then developing the picture by means of any of my improved solutions or other suitable developers.

The said Invention also comprises improved developing solutions to be applied to paper or other surfaces which have been coated with platinous and ferric salts.

These improved developing solutions may be applied to the paper or other material which previous to its exposure to light has been coated with ferric and platinous salts mixed in the proportions hereinafter specified or in different proportions and with or without the addition of a salt of lead or of mercury. One distinguishing feature of my present invention is the comparatively large quantity of platinous salt used in coating the paper or other material, that is to say, in my present improved process I do not employ less than one and seven tenths (1.7) of a grain of the platinous salt for each square foot of surface to be coated, and I prefer to use a much larger quantity, usually as much as four (4) grains of such salt, and sometimes more, for each square foot of coated surface, whereas in the practice of the Invention described in the said former Specification the quantity of platinous salt used did not exceed two thirds ($2/3$) of a grain for each square foot of the surface coated.

By the use of such greatly increased quantity of platinous salt in the coating I obtain results greatly superior to those obtained by the process described in my said former Specification. I also obtain results superior to those

obtained by the improved process described in the Specification of my Patent dated 12th July, A.D. 1878, N^o 2800, while obviating the necessity for the addition of a platinous salt to the developing solution as described therein, and thus simplifying the process.

The platinous salt I prefer to employ is the potassic chloro-platinite. I use this salt in such proportion or quantity that each square foot of the surface will receive, when coated, not less than one and seven tenths (1.7) of a grain thereof, but usually a much greater quantity, that is to say, about four (4) grains of the salt, and sometimes more. The iron salt I prefer is the ferric oxalate.

The platinous salt and the iron salt may be mixed in the desired proportions, and dissolved in a suitable quantity of water, and then applied to the paper or other surface, or the solutions of these salts may be applied separately. I prefer to use for ordinary purposes an aqueous solution containing in each fluid ounce sixty (60) grains of potassic chloro-platinite and sixty (60) grains of ferric oxalate for application to the paper or other suitable surface. I do not confine myself to this proportion, but may use less or more, according to the result desired to be obtained. The solution is applied to the paper or other surface by means of a pad of cotton wool or flannel, or the paper may be coated with it by any of the means known to photographers.

The paper thus coated is after being dried ready for use, and after its exposure to light under or behind a negative I apply to it a developing solution containing potassic oxalate or either of my improved developing solutions. The developing solution of potassic oxalate is made by dissolving one hundred and twenty (120) grains or more of the salt in one fluid ounce of water. As soon as the print has been developed by means of this solution I wash it, first in a weak solution of acid, preferably citric acid, and afterwards in water.

I prepare an improved developing solution as follows, that is to say :— I use for this solution the tartrate or citrate of soda, of potash, or of ammonia, or any compound of any of these salts with each other. Or I use acetate of soda, of potash, or of ammonia or the monoammonic, the diammonic or the monosodic ortho-phosphates; I prefer however to use the citrate of soda. I use one or more of the above named salts or mixtures of these salts, or other salts which will serve the same purpose, alone or mixed with the salts of platinum or of iridium, as described in the Specification of my said former Letters Patent, N^o 2800.

I apply the developing solution thus prepared to the paper or other surface coated according to the first part of my present Invention with platinous and iron salts or to the surfaces that have been coated with platinous and iron salts used in proportions different from those specified in the said first part of my Invention; I also apply the said developing solution to paper or other surfaces that have been previously coated with platinous salts, ferric oxalate, and salts of lead or mercury as described in the Specifications of my former said Patents.

I prepare this developing solution as follows, that is to say :— I make a solution containing one hundred and twenty (120) grains of citrate of soda in one ounce of water, of a sufficiently strong solution of either or any of the other salts above specified. This solution may be applied to the prepared paper or other surface by pouring it over the same, or by immersing the paper therein, or by floating the paper thereon. It may be applied cold, warm, or hot,

but preferably hot. The strength of the solution may be varied, but the best results will usually be obtained by a strong or saturated solution. To this solution of citrate of soda or of any or either of the other salts I may, as above specified, add a salt of platinum or of iridium, as specified in the Specification of my said former Patent. I prefer the potassic chloro-platinite for this purpose.

VII.4 N° 1681, February 2nd, 1887**Improvements relating to Photo-chemical Printing.**

My invention has for its object the production, upon paper or other surfaces, of photographic pictures or images in platinum, that is to say, pictures of images of which the colouring matter or pigment is platinum. It differs from the processes of photo-chemical printing described in the specifications of my former patents, viz. :— N° 2011 dated June 5th, 1873, N° 2800 dated July 12th, 1878, and N° 1117 dated March 15th, 1880, in which processes (as far as they relate to platinum) the paper or other surface is coated with a solution of a salt of platinum and sometimes other salts and also with a solution of ferric oxalate. These solutions are applied, either separately or mixed, to the paper, and in all cases the sensitive coating of the paper contains a salt of platinum and ferric oxalate. After exposure to light, the prepared surfaces are treated with one or other of the developing solutions described in the said Specifications.

Hitherto no means have been known by which the salt of platinum could be employed entirely in the developer or developing solution, instead of wholly or partly in the sensitive coating of the paper or other surfaces as above set forth. I have, however, now discovered a process by which I can accomplish this result. For this purpose I apply to paper or other suitable material which has been rendered sensitive by a coating of ferric oxalate and afterwards exposed to light, a developer containing salts of platinum and certain soluble phosphates (or other salts, in which the ferrous oxalate image produced by exposure to light is insoluble or nearly so), with or without the addition of potassic oxalate, potassic tartrate, ammoniac citrate or other salts which tend to increase the rapidity and vigour of the development. By this process I avoid the necessity of using salts of platinum in the sensitive coating of the paper or other surface. I thereby greatly diminish the cost of the process and can gain good results without heating the developer.

Moreover I obtain a slower developing action so that it is possible to watch the progress of development and to arrest it at any desired moment by washing the print in a solution of acid.

According to my present invention I use paper, wood, woven fabric or other material the surface of which I prepare and render sensitive for photographic purposes by the application of a coating or coatings containing ferric oxalate with (or without) the addition of a salt of lead or of mercury, or mixtures thereof, and without any salt of platinum.

I first prepare the paper or other surface by the use of this coating as hereinafter specified. I then expose it to light under or behind a negative and then develop the picture by means of one of my improved developing solutions hereinafter specified, or other suitable solution containing a salt of platinum. For preparing or coating the paper or other material, I employ for ordinary purposes an aqueous solution of ferric oxalate containing in each fluid ounce about sixty (60) grains of ferric oxalate; but I may use less or more of the latter according to the result desired to be obtained. I am of course aware that there are other salts of iron sensitive to light, but the oxalate is the best for my purpose. I sometimes mix or dissolve in the ferric oxalate a salt of mercury or of

lead or of a mixture of these salts; for instance, I dissolve in one fluid ounce of the ferric oxalate solution above described, from one grain to three grains of mercuric chloride. Or I apply a solution of a salt of lead or mercury or a mixture of these salts to the paper or other surface either previously or subsequently to coating the same with ferric oxalate. I find the mercuric salt very useful where a warm tone or effect somewhat resembling sepia is desired.

I do not confine myself to aqueous solutions of the above named salts.

The paper thus coated, after being dried, is ready for use. If two coatings are applied to the paper or other surface; it should be dried between the application of the first and second coatings. After its exposure to light under or behind a negative, I apply it to the developing solution.

I prepare an improved developing solution or developer as follows, that is to say:— I use solutions of various soluble phosphates. I have been most successful with the following, viz. :— the monosodic or disodic, the monopotassic or dipotassic or the mono-ammonic or diammonic orthophosphates, or mixtures or combinations of these salts with one another, and with or without the addition of other salts such as potassic oxalate, ammoniac citrate and others. In all cases I add to these solutions or mixtures of solutions a salt of platinum. I mix a solution of this salt with the above named solutions or I dissolve the platinum salt in them. The platinum salts most suitable for my purpose are the ammoniac, potassic and sodic chloro-platinites, the ammoniac, potassic and sodic bromo-platinites or mixtures of them, and in some cases I use a very small quantity of a platinum salt, such as ammoniac, potassic or sodic chloro-platinate.

I usually prepare this developing solution as follows, that is to say :— I dissolve in one fluid ounce of water, one hundred (100) grains of di-potassic orthophosphate, forty (40) grains of potassic oxalate and ten (10) grains of potassic chloro-platinite ; or I may make it in another manner, viz. : by dissolving in one fluid ounce of water, one hundred (100) grains of diammonic orthophosphate, thirty five (35) grains of ammoniac citrate and ten (10) grains of ammoniac chloroplatinite; or I make similar developing solutions with the salts previously mentioned. I make also developers containing only phosphates and salts of platinum, that is to say, I may make a developer by dissolving in one ounce of water, about one hundred (100) grains of monopotassic or di-potassic orthophosphate or mixtures of these salts and ten (10) grains of potassic chloro-platinite.

The developing solution is applied to the paper or other surface (after the same has been exposed to light) by pouring it over the same, or by immersing the paper therein, or by floating the paper thereon, or by means of a brush or otherwise. It is applied cold, warm or hot as desired. A cold solution usually takes longer to effect the development of the picture than a hot one. The strength of the solution may be varied; usually the best results are obtained by strong solutions of the phosphates and other salts; the platinum salt will ordinarily be used in the proportion of from five to ten grains of the salt to one fluid ounce of the developer.

Having now particularly described and ascertained the nature of my said invention, and in what manner the same is to be performed, I wish it to be understood that I claim—

First. The process or method in which I sensitize the surface of the paper or other material by the means herein specified, then expose the surface to light and then develop the picture or image by the use of a solution containing a salt of platinum, as above set forth.

Second. The production or development of photographic pictures or images in platinum by the application of a salt of this metal to a surface which has been previously rendered sensitive by the application of a ferric salt and exposed to light.

Third. Paper or other material which has its surface prepared and rendered sensitive for photographic purposes by the application of a ferric salt and a salt or mercury or of lead or of both mercury and lead as above set forth.

VII.5 No 16,003, November 21st, 1887**Improvements relating to Photo-chemical Printing.**

My invention has for its object the production of photographic pictures or images in platinum, by improved methods of carrying into effect the process described in the specification of my former Letters Patent dated February 2nd A.D. 1887 No. 1681.

By the said process I have been enabled to produce pictures of excellent quality and to greatly diminish the cost of the platinotype process and obtain other important advantages. I have, however, found that I do not in using the process, as described in the said former specification in all cases, obtain an absolute uniformity of tone or colour or monochromatic effect in the picture, that is to say, although the shadows will be of a pure black tone, there will be sometimes a slight trace of brown in the high lights of the developed picture. This is a defect which does not impair the value of a photographic print in respect of accuracy and other qualities, but the presence of two colours may be considered offensive to good taste. In the picture of a landscape for instance, it is generally conceded that the foreground shadows should be warmer in tone or colour than the high lights and delicate distance, or certainly not colder.

Now although I have not succeeded in producing pictures in which the darker parts or shadows are warmer in tone than the lighter and more delicate portions or high lights, yet I have as one result of my present invention provided for carrying into effect the said process with the certainty that the tone or colour shall be uniform throughout, that is to say, I can be sure that no part shall be of a warmer tint than another part of the picture.

The process described in the specification of my said patent No. 1681 is distinguished from former processes of mine chiefly by the fact that the platinum is contained entirely in the developing solution, that is to say, I described a surface coated with ferric oxalate (with or without a salt of lead or of mercury and without any platinum) and the use, for developing the image or picture thereon, of a solution containing a salt of platinum in all cases mixed or combined with a phosphate or other salt in which the ferrous image is insoluble, and sometimes with other salts. I now find, however, that, by ensuring the presence or contact of a salt of mercury or of lead with the image at the time of its development, I obtain a better reducing action and avoid the necessity for using in the developing solution phosphates or other salts for rendering the ferrous image insoluble, the presence of which salts, as far as I have been able to observe, is the cause of, or is accompanied by the defect in the tone or colour of the picture.

I therefore now proceed according to the following method, that is to say, I coat paper or other material with ferric oxalate together with a salt of mercury or of lead or both. Then I expose the coated surface to light under or behind a negative or other suitable screen, and then develop the ferrous image produced by the action of light, with a solution containing a salt of platinum together with a salt of oxalic or citric or tartaric acid, or mixtures of these, or together with other substances which aid in the reduction of the metal from the salt of platinum by the ferrous image produce as aforesaid.

Or I adopt the following method, viz. ;— I use a surface sensitized by ferric oxalate alone and then, after exposure to light, develop the picture or image with a developing bath or solution containing one or more of the above named salts or substances which aid in the reduction of platinum in the manner aforesaid, together with a salt of platinum and also a salt of lead or of mercury or both, but in this case preferably the salt of lead.

It will be observed that the lead or mercury, one or the other of which is in all cases essential in the practice of my invention, is in the one case present in the sensitive coating of the paper before its exposure to light, and in the other case is wholly in the developer. But for some purposes I use a salt of mercury or of lead both in the sensitive coating of the paper and in the developer.

In practising my invention according to the first method above described, I coat the paper or other surface with ferric oxalate (or with a compound or mixture of the same and other oxalate of an alkali metal) together with a salt of lead or of mercury or of both. The salts of lead which I find best for my purpose are the nitrate and chloride. If I use salts of mercury, I employ only the mercuric salts, and of these I prefer mercuric chloride. The ferric oxalate and the lead or mercury salt can be applied together in one solution, or the said salts can be applied separately in solution to the paper or other surface. I usually apply them in one solution. When they are applied separately, the paper or other surface should be dried between the coatings.

In some instances, I employ an aqueous solution of ferric oxalate containing in each fluid ounce about sixty (60) grains of the oxalate $\text{Fe}_2(\text{C}_2\text{O}_4)_3$ more or less according to the result desired to be obtained. And I add to, or dissolve in each ounce of this solution one (1) grain of plumbic chloride and one (1) grain of mercuric chloride.

I sometimes omit the lead salt from this solution and increase the quantity of the mercuric salt, that is to say, instead of one (1) grain of mercuric chloride I use two or more grains of this salt.

The paper thus coated, after being thoroughly dried, is ready for use. After its exposure to light under or behind a negative or suitable screen, I apply to it the developing solution.

I prepare this developing solution with potassic oxalate and potassic chloro-platinite as described in the specification of my former Letters Patent No. 2800 A.D. 1878. I prefer to use an aqueous solution of these salts containing in each fluid ounce about ninety (90) grains of potassic oxalate and nine (9) grains of potassic chloro-platinite.

Or I use, for developing, an aqueous solution containing in each fluid ounce about sixty (60) grains of ammoniac tartrate and eight (8) grains of ammoniac chloro-platinite.

Or I make developing solutions with any of the other salts or substances hereinabove mentioned as applicable for this purpose, or with other salts which tend to aid in the reduction of the platinum salt by the ferrous image produced by the action of light. In practising my invention according to the second method hereinbefore specified, I first apply to the paper or other surface a coating of an aqueous solution containing about sixty (60) grains of ferric oxalate in each fluid ounce of solution. I then dry the coated paper and then,

after exposing it to light under or behind a negative, I apply to it the developing solution.

For this developing solution I sometimes employ an aqueous solution containing in each fluid ounce about ninety (90) grains of potassic oxalate and nine (9) grains of potassic chloroplatinite. To this solution I add a solution of a salt of lead, preferably the acetate, until a permanent precipitate begins to form. If I use a salt of mercury instead of a salt of lead I prefer the mercuric chloride of which I dissolve (or add) about five (5) grains in each fluid ounce of the said solution. The salts of mercury do not in all cases ensure a monochromatic tone in the picture, but in other respects they afford good results.

Or I use a developing solution containing a salt of platinum and a salt of lead or of mercury and one or more of the other hereinbefore specified salts of oxalic, citric and tartaric acids or substances, but when a salt of lead is employed, there must be no salt used in the developer which would entirely prevent the solution of the lead salt. These developing solutions containing lead or mercury salts or both can also be used for developing photographic pictures or images on paper and other surfaces which have been coated with ferric oxalate together with a salt of lead or of mercury.

I sometimes apply the constituents of the developer separately or in two solutions to the sensitive surface after it has been exposed to light. In this modification of my process, I first apply a solution of plumbic acetate or of mercuric chloride to the said surface and then quickly, without washing or drying the surface, apply to it in solution the remaining constituents or ingredients of the developer. The developing solutions mentioned in this specification I prefer to apply cold, but occasionally I apply in a heated state such of them as are not decomposed by heat. The salts of platinum which I prefer to make use of in the developers herein described are the platinous salts viz. :— the ammoniac, potassic and sodic chloroplatinates, the ammoniac potassic and sodic bromo-platinates, or mixtures thereof; but in some instances I use a small quantity of a platinum salt such as ammoniac, potassic or sodic chloroplatinate. The coating and developing solutions are applied as described in my former specifications or by other suitable means.

Having now particularly described and ascertained the nature of my said invention, and in what manner the same is to be performed I wish it understood that I do not limit myself to the proportions above stated nor do I limit myself to the use of aqueous solutions for the purposes of forming the coating or sensitizing and developing solutions as I may use any suitable solvent for the salts employed in my process, and I claim :—

First. The method or process of photo-chemical printing wherein I modify or vary the process described in the specification of my said Patent No. 1681 by ensuring the presence or contact of a salt of lead or of mercury with the image during the development and by avoiding the use of phosphates, or other salt in which the ferrous image is insoluble, as, and for the purpose, herein set forth.

Second. The development of a photographic picture or image by a solution (which contains a salt of platinum and which does not contain any phosphate) applied to a surface sensitized by the application of a solution containing ferric oxalate and a salt of lead or of mercury or both, as above set forth.

Third. The development of a photographic picture or image by a solution (which contains a salt of platinum together with a salt of lead or of mercury and which does not contain a phosphate) applied to a surface that has been sensitized by a solution containing ferric oxalate with or without a salt of lead or of mercury, as above set forth.

VII.6 Nº 20,022, September 4th, 1913**Improvements in or relating to Photographic Printing & Paper therefor.**

This invention consists in improvements in or relating to photographic printing and paper therefore, and the expression "paper" in this specification is used to include paper, textile fabrics, wood, and other surfaces suitable for receiving photographic prints.

The principal object of this invention is the production of photographic printing paper having a coating or surface sensitive to light and containing salts of iron, silver and platinum, which paper after exposure to light under a negative and subsequent development shall yield an image composed of silver and platinum, the platinum constituent of such image being variable in quantity in some proportion to the amount of platinum salt used in the sensitive coating of such paper.

Thus the said paper may be produced either so as to give images composed of silver with very little platinum or images composed of silver with an increased proportion and quantity of platinum. And in practice the quantity of platinum in the image may advantageously be so increased until a point is reached where such image may be considered permanent. The point may be defined as the point where the image in platinum remaining after the silver content of the original silver and platinum image has faded, or has been removed, will of itself satisfactorily represent the gradation and retain all of the detail which existed in the original silver and platinum image before its silver content had faded or had been removed.

A further object of this invention is to secure such permanent residual images in platinum as hereinbefore described by the employment of a quantity of platinum salt in the coating of the said printing paper less than that used in the platinotype process.

And other objects of the invention are that such photographic printing paper shall be easy of manipulation in weakened ordinary daylight ; shall require only moderate exposure to light and shall remain in good condition during storage; and further that the images produced on such paper shall require no subsequent toning.

This invention is based on the discovery that I have made that the reduction of chloride of silver by a solution of ferrous oxalate in potassium oxalate is greatly facilitated, increased in rapidity and made more complete, by placing in contact with this silver salt a small quantity of potassium chloro platinite before the reducing agent (ferrous oxalate) is applied to the silver salt. And I have found that the only salts of platinum of value in thus aiding in the reduction of silver chloride by ferrous oxalate are salts of chlorine and of platinum that is to say chloro platinites or chloro platinates, salts which are also described as platino-chlorides and platinichlorides. And I also find platinic chloride to be of value. The salts of platinum just named are themselves reducible by a solution of ferrous oxalate and when one of these salts is used as above described to aid in the reduction of silver chloride it will be reduced together with the silver salt and both platinum and silver will be liberated. This

effect of platinum salts in aiding the reduction of silver chloride can be easily shown by a purely chemical method but perhaps more readily by a practical trial on paper in the manner following: If the paper is first of all coated with silver chloride and then with ferric oxalate, then exposed to light under a negative and then developed in oxalate of potash yields only a poor image, but if in addition to the silver chloride and ferric oxalate the coating is made to contain a small quantity of potassium chloro platinite, then on exposure and development a stronger image of blackish colour will be obtained; and it has been proved that the intensity of this image is due mostly to the increased reduction of the silver salt and only slightly to the reduction of the small quantity of platinum salt used in this experiment. One of the methods in which this discovery is applied in this invention to the production of an improved photographic printing paper is as follows:—

The paper first of all receives a coating of chloride of silver which may be applied or attached to the surface as an emulsion in gelatine or other suitable medium or formed on the surface by the well known process of double decomposition. This coating of silver chloride should be free from other salts of silver. The coated surface is then again coated with a solution of ferric oxalate in which is dissolved some potassium chloro platinite (K_2PtCl_4). After the paper has been dried, it is exposed to light under a negative. The action of light through the negative forms on the sensitive coating of the paper a faint image consisting mainly of ferrous oxalate. This exposed paper is now immersed in a solution of oxalate of potash which quickly commences to dissolve the ferrous oxalate forming the image, but this solution of ferrous salt in oxalate of potash is a strongly reducing agent. Now salts of silver and platinum are in contact with the ferrous image on the paper and as this ferrous image is dissolved by the application of oxalate of potash, the resulting solution of ferrous salt reduces these salts of silver and platinum “in situ” forming or yielding an image composed of silver and platinum more or less in the metallic state and coinciding with the position of the original image of ferrous oxalate. This final image composed of silver and platinum is of a black tone agreeable to the eye and does not require toning. All that now remains is to dissolve out the unaltered salts from the paper in any suitable way.

In the production of this photographic printing paper it is essential to the invention that the salt of silver employed shall be the chloride and not a salt of silver like the nitrate and others which will decompose the platinum salt.

In my previous patent No. 2011 of 1873 the object of which was to obtain photographs or pictures in which the image should consist of platinum, iridium or gold the final specification (Example 2) gave a method somewhat similar to the method described in this invention.

In that method paper was coated with nitrate of silver.

In practice it was found that the developed images on such paper contained very little metallic platinum, that they were very variable in quality and often required subsequent toning to render them of value. The process was unsatisfactory and was quickly abandoned. The most important distinction between the method employed in 1873 and that used in this invention lies in the fact that in the 1873 method of coating paper the platinum salt is

decomposed by nitrate of silver, whereas in this invention the platinum salt and silver chloride do not suffer material mutual decomposition and remain as such in the finished paper prior to the process of development.

The following is a description of one of the methods adopted for coating paper according to this invention.

I first apply to a sheet of plain paper such as is made for the platinotype process, a coating of silver chloride by the well know method of double decomposition the solutions used for this purpose being potassium chloride and silver nitrate.

The potassium chloride must be in excess so as to secure a complete decomposition of the silver nitrate. The potassium chloride solution is made by dissolving 5 grammes of potassium chloride in 100 cubic centimetres of water and the silver nitrate solution is made by dissolving 5 grammes of silver nitrate in 100 cubic centimetres of water. After the coating of silver chloride has been formed on the paper by the use of these solutions the paper surface is usually washed in water in order to remove the soluble salts.

But instead of applying this coating of silver chloride to the paper by the method of double decomposition I sometimes make use of an emulsion of chloride of silver in gelatine or other suitable medium and apply such emulsion to the paper by one of the usual and well known methods.

The second coating solution now to be applied to the paper I prepare by dissolving a small quantity of potassium chloro platinite in a solution of ferric oxalate, this ferric oxalate being such as is usually employed in the platinotype process.

Now in order to prepare the second coating solution I dissolve in 500 cubic centimetres of the ferric oxalate solution one gramme or less up to six grammes or sometimes more of potassium chloro platinite. If the object is to form the image mainly of silver I dissolve say one gramme of potassium chloro platinite in the ferric oxalate solution but if the object be to make an image which will have or contain a permanent residual image of platinum I dissolve say six grammes of this salt in 500 cubic centimetres of the ferric oxalate solution. The second coating solution is applied either by brushing the solution over the paper previously coated with the silver chloride or by floating the paper on the solution or by other suitable means.

The coating is finally well dried in a current of warm air or before a fire or in any suitable way.

The paper thus coated is now ready for use. It is first of all exposed to light behind a negative or other suitable screen and then immersed in a developing solution, made by dissolving one pound of potassium oxalate in 64 ozs. of water. In about one minute development is usually complete. The developed print is then moved to a clearing bath made thus

Potassium bisulphate	3 ozs.
Potassium oxalate	0.5 ozs.
Water	100 ozs.

In this bath it should remain from ten to fifteen minutes and then it is well washed in several changes of water. Finally the print is "fixed" in a "hypo"

solution made by dissolving one ounce of sodium "hyposulphite" in ten ounces of water. The print is finally washed in several changes of water.

Other methods and salts may be used for developing and clearing or "fixing" the prints but the method above is an excellent one. In preparing the said photographic printing paper I sometimes vary the operations described above or invert their order, that is to say, I may change the order in which the various salts are applied to the paper. For instance, instead of applying the potassium chloro platinite salt mixed in solution with ferric oxalate I sometimes apply the potassium chloro platinite dissolved in water or in any suitable solvent as a separate coating which I apply usually between the coating with silver chloride and the coating with ferric oxalate.

And I sometimes employ for coating the paper an emulsion of silver chloride in a suitable medium in which is dissolved the requisite quantity of platinum salt and of ferric oxalate.

I sometimes apply the sensitive coating to other surface than paper, for instance to cotton or linen fabrics, to silk fabrics, to wood, &c.

In preparing the said photographic printing paper or other surface I sometimes employ other salts than those named for instance in the coating of the paper I may use the bromide of silver instead of the chloride of silver but I usually prefer the latter salt. And instead of the potassium chloro platinite I sometimes use the sodium or ammonium chloro platinite or other suitable chloro platinites or the potassium, sodium or ammonium chloro platinate or platinic chloride but of these salts I prefer as the most generally useful the potassium chloro platinite. And instead of a solution of ferric oxalate I sometimes employ a solution or solutions of the double salts of ferric oxalate with potassium sodium or ammonium oxalate or other suitable oxalate, or a solution of ferric citrate or its double salts, or mixtures of solutions of any of these with a solution of ferric oxalate; these solutions are hereinafter referred to as equivalents of ferric oxalate.

And in the formation of the coating of silver chloride on the paper by means of double decomposition I do not confine myself to the salts named in the above described process, namely potassium chloride and silver nitrate but I may use other salts which by their mutual decomposition will precipitate silver chloride. I do not restrict myself to the exact proportions or quantities of the chemical salts used in the above described process, as these proportions and quantities may be varied within certain limits according to the results desired to be obtained or to other conditions.

I do not confine myself to the use of aqueous solutions of the chemicals hereinbefore referred to, as these salts may be dissolved and used with any suitable solvent. I have further found that particularly advantageous results can be obtained in the above process by using paper the surface of which has been parchmented by treatment with acid or by other well known means. The paper is coated or treated on each side with sulphuric acid sufficiently strong to attack the paper; the paper is well washed in water to free it from acid and is then dried. The acid is not left on long enough to penetrate the paper, the aim being to get a film of altered paper on each side.

In a further modification of the photographic printing process according to this invention, the platinum salt may be wholly or in part contained in the developing solution, that is to say, the coating of chloro platinite or chloro platinate may be omitted from the paper or may be reduced to a minimum and the paper, after exposure may be treated with a solution of the chloro platinite or chloro platinate in admixture with the developing solution.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. The hereindescribed process for the production of photographic printing paper in which the paper is coated with silver chloride, with a chloro platinite or chloro platinate or platinic chloride, and with ferric oxalate or its equivalent.

2. Photographic printing paper coated with silver chloride, a chloro platinite or chloro platinate or platinic chloride and ferric oxalate or its equivalent.

3. The modification of the subject matter of Claims Nos. 1 and 2 in which the paper in the first place is partly parchmented so as to obtain a film of altered paper on both surfaces, for example by treating it on each side with sulphuric acid sufficiently strong to attack the paper after which the paper is washed in water to free it from acid, and dried.

4. The photographic printing process in which paper treated as specified in Claims Nos. 1, 2 or 3, is exposed to light behind a negative or other suitable screen, and thereafter developed, cleared and fixed, substantially as described.

5. The modification in the subject-matter of the preceding claims, in which silver chloride is replaced wholly or in part by silver bromide.

6. The modification in the subject-matter of the preceding claims in which the platinum salt is wholly or partly contained in the developing solution.

APPENDIX VIII

Conversion of Obsolete Units of Measurement

When interpreting 'historic' formulations, it is advisable to convert all units of weight to grams (g), and all volumes to cubic centimeters (cc or cm³). Note that the volume measurement of 1 litre (now defined as 1000 cc or ml) is referred to as a cubic decimeter (dm³) in the SI. The following conversions may be useful.

VIII.1 Weight

Apothecaries' measure was used by early physicians and scientists for weighing out solids and making up formulae:

1 grain (gr)					
1 scruple (scr)	= 20 grains		=	0.0648 g	
1 drachm (dr)	= 3 scruples (60 grains)		=	1.296 g	
1 ounce (oz)	= 8 drachms (480 grains)		=	3.888 g	
1 pound (lb)	= 12 ounces (5760 grains)		=	31.104 g	
			=	373.242 g	

Troy weight has the same basis as Apothecaries measure, the grain, and was always used for weighing precious materials such as gold and silver metal:

1 grain Troy	= 1 grain Apothecaries				
1 pennyweight	= 24 grains		=	0.0648 g	
1 ounce	= 20 pennyweights (480 grains)		=	1.555 g	
1 pound	= 12 ounces (5760 grains)		=	31.104 g	
			=	373.242 g	

The 'carat' ('karat' in the USA) was used to denote the number of parts of gold by weight per 24 parts of metal or gold alloy. Thus, 24 carat gold is 100%, 12 carat is 50% gold. Confusingly, 'carat' can also denote a unit of weight for precious stones, where: 1 carat = 0.200 g.

Avoirdupois measure was the common system for weighing and selling solids; it was adopted by the British Pharmacopoeia in 1864:

1 grain	= 1 grain Apothecaries				
1 ounce	= 437.5 grains		=	0.0648 g	
1 pound	= 16 ounces (7000 grains)		=	28.3495 g	
			=	453.592 g	

The larger units in the Avoirdupois system – stones, quarters, hundredweights, and tons – are omitted as irrelevant here. Texts do not always make clear which system the 'ounces' (abbreviated 'oz.') in their formulae refer to, but they are more likely to be Avoirdupois, which was widely used by the 1850s, unless the substance was metallic gold or silver, when Troy ounces were appropriate. As a consequence of this ambiguity, an 'ounce' of silver nitrate weighed less than an 'ounce' of silver metal! Avoirdupois measure also defined a "dram" (usually so spelt to distinguish it from the Apothecaries drachm) of 1/16 ounce.

VIII.2 Volume

British fluid measure was used for measuring volumes of liquids. The Imperial pint of 20 fluid ounces replaced the ancient 16-ounce pint in 1826:

1 minim	= (ca. 1 drop)	= 0.0592 cm ³
1 fluid drachm	= 60 minims	= 3.552 cm ³
1 fluid ounce	= 8 fluid drachms	= 28.413 cm ³
1 gill	= 5 fluid ounces	= 142.065 cm ³
1 pint	= 20 fluid ounces	= 568.261 cm ³
1 quart	= 2 pints	= 1136.522 cm ³
1 gallon	= 8 pints	= 4546.087 cm ³

1 fluid ounce of water weighs approximately 1 ounce avoirdupois. Many C19th workers described their solution strengths in grains per fluid ounce:

A concentration of 1 grain/fluid ounce = 2.28 g/dm³ = 0.228 % w/v

A unit of volume occasionally used was the cubic inch = 16.387 cm³

US fluid measure differs from British liquid volume measurement in the size of its basic unit, the minim, and the US system still retains a 16-ounce pint today:

1 minim (USA)	=	0.06161 cm ³
1 fluid dram (USA)	= 60 minims	= 3.697 cm ³
1 fluid ounce (USA)	= 8 fluid drams	= 29.574 cm ³
1 pint (USA)	= 16 fluid ounces	= 473.176 cm ³
1 quart (USA)	= 2 pints	= 946.352 cm ³
1 gallon (USA)	= 8 pints	= 3785.412 cm ³

VIII.3 Area

Willis referred to paper area in square feet or square inches (1 ft² = 144 in²):

$$1 \text{ square foot (ft}^2\text{)} = 0.09290304 \text{ m}^2$$

$$1 \text{ square inch (in}^2\text{)} = 6.4516 \text{ cm}^2$$

so a coating weight of:

$$1 \text{ grain/ft}^2 = 0.6975 \text{ g/m}^2$$

Note that the unit conversion to SI gives:

$$1 \text{ g/m}^2 = 100 \text{ } \mu\text{g/cm}^2$$

APPENDIX IX

Glossary

Text in **bold face** refers to another Glossary entry

Acid

A substance releasing hydrogen **ions** (H^+) in **aqueous** solution. Acidic solutions have a **pH** value less than 7.

Actinic

Of radiation or light capable of bringing about a chemical reaction; usually confined to the **ultraviolet** and light of short wavelengths (blue and green).

Albumen

The clear white of hens' eggs: a 10% solution of ca. 40 different proteins (macromolecular polypeptides). Used as a colloidal binder for photographic printing paper of the same name.

Alkali

A substance releasing hydroxide **ions** (OH^-) in **aqueous** solution. Some alkalies achieve this by removing hydrogen **ions** from water and binding them, so leaving excess hydroxide **ions**. Alkaline solutions have a **pH** value greater than 7.

Alum

Double salts of aluminium sulphate with alkali metal **cations**; the comonest is potassium aluminium sulphate dodecahydrate, $KAl(SO_4)_2 \cdot 12H_2O$. Chiefly used in photography and papermaking for hardening coatings of **gelatin**.

Aluminosilicate

A group of minerals containing aluminium and silicon linked by oxygen, and sometimes metal **cations**; typically "clays" such as **kaolinite**.

Ambient

Referring to the properties of the surrounding environment; e.g. its temperature, or **Relative Humidity**.

Amorphous

A solid not possessing a regular crystalline structure, e.g. a glassy substance.

Aniline process

A positive-working reprographic process invented by William Willis Senior, in which acidified dichromated paper (due to Mungo Ponton) is the photosensitive component. On development with aniline (aminobenzene) or toluidine the residual dichromate oxidises it to blue-black dyestuffs.

Anion

A negatively-charged molecule or atom; arising through gain of **electron(s)** by the neutral entity. It must co-exist with an equal but oppositely charged atom or molecule; see **cation**. The charge on an anion is always a whole number, written with a superscripted n- (minus) sign, where n is the number of units of charge of the **electron**.

Aqua regia

(Latin: “Royal water” so-called because it is capable of dissolving the “royal” metal, gold.) A mixture of concentrated hydrochloric acid and concentrated nitric acid, in the approximate volume proportions of 3:1.

Aqueous

Watery; usually referring to a **solution** of a substance in water.

Argentotype

A **siderotype** process invented by Sir John Herschel in 1842 in which the **photoproduct** from exposure of ammonium ferric citrate reduces silver nitrate to **nanoparticle** silver metal, which constitutes the image.

Atom

The smallest neutral (uncharged) particle of a chemical element that retains the essential identity of that element, the **atomic number**.

Atomic Number

A sequential number allocated to each element, when they are ordered in the series of ascending **atomic weight** (approximately). More exactly, it is numerically equal to the number of **protons** in the atomic nucleus and therefore also equal to the number of orbiting **electrons** in the neutral **atom**.

Atomic weight

The weight (strictly, mass) of an **atom** of an element on a scale relative to the carbon atom having a value of 12.0000. On this scale the oxygen atom has a value of 16.000 and the hydrogen atom 1.008. Now called the **relative atomic mass**.

ATR

Attenuated Total Reflectance – for obtaining spectra (UV-Vis or IR) from the surfaces of solids e.g. paper. Cf. Diffuse Reflectance

Baryta

Barium sulphate, BaSO₄, a dense white pigment used in photographic papers.

Base

A substance that reacts with an **acid** to give a **salt**, plus water. All **alkalies** are bases, but not all bases are significantly alkaline (e.g. some water-insoluble metal oxides).

Buffer

A substance (or mixture of substances) that helps to maintain a fixed, pre-determined **pH**. The pH value of its solution is only slightly affected by the addition of moderate amounts of either **acid** or **alkali**.

Carbon print

A photographic printing process using photohardening by a dichromate of a **colloid** – usually **gelatin** – containing a pigment – sometimes lampblack (carbon), but it can be pigment of any colour.

Catalyst

A substance that accelerates a chemical reaction, but is left unchanged at the conclusion of it. The process is called catalysis.

Cation

A positively-charged **molecule** or **atom**; arising through removal of **electron(s)** from the neutral entity. It is written with a superscripted $n+$ sign, where n indicates the number of units of the charge of the **proton** that are present (equal and opposite to the charge of the **electron**). See **anion**.

Cellulose

The chief constituent of plant cell walls and therefore of cotton fibers. It can be obtained from materials such as wood pulp, cotton and flax. Chemically, it is a polysaccharide of formula $(C_6H_{10}O_5)_n$, where $n \sim 15,000$.

Celsius

The temperature scale also known as Centigrade, which has now replaced the Fahrenheit scale throughout the world, except in the USA. The conversion formulae are

$$C = 5(F-32)/9$$

$$F = 32 + 9C/5$$

Pure water freezes at 0°C (32°F) and boils at 100°C (212°F), under normal atmospheric conditions. Normal room temperature is ca. 20°C (68°F).

Chelate

A metal compound, or **complex**, in which the metal **cation** is bound by a **ligand** via two or more atoms of the same **molecule**. It derives from the Greek word for 'crab's claw'. **Oxalate** can act as a bidentate chelating ligand.

Chrysotype

A **siderotype** process invented by Sir John Herschel in 1842 in which the **photoproduct** from exposure of ammonium ferric citrate reduces gold chloride to gold metal, which constitutes the image.

Citrate

An organic **anion** derived from citric acid, $C_6H_8O_7$, which is tribasic, i.e. it can lose up to three **hydrogen ions** in forming **salts**.

Clearing

A term used to denote the removal from a photographically printed image of all the excess unreacted chemicals, and reaction products, other than the image substance. It is essentially the same as fixing or fixation.

cm³

Abbreviation for cubic centimeter. An SI measure of volume. Also written as cc. It is now effectively identical with a millilitre or ml., since the litre was redefined in 1964 as 1000 cc.

Coating volume, specific

The volume of liquid taken up per square meter of a paper sheet, under specific conditions of coating, usually in units of cm^3/m^2 ; the liquid is commonly a photosensitizer solution.

Coating weight

A measure of the surface concentration of a substance (e.g. a sensitizer or image pigment) as the mass per unit area of a paper sheet (or other substrate). The standard unit is grams per square meter, g/m^2 . It is numerically approximately the same as the specific coating volume.

Cobb value

The absorptivity of water by a paper sheet under specified conditions of pressure, temperature and time: the weight of water taken up by a sheet in contact with pure liquid water is expressed in grams per square meter of surface, g/m^2

Collodion

A solution of cellulose nitrate dissolved in a 60:40 mixture of diethyl ether and ethanol. The soluble variety of cellulose nitrate is called "pyroxylin" and is less than fully nitrated, which is the case with the explosive, guncotton, which is the tri-nitrate. Collodion is used as a binder layer for photographically sensitized plates and papers.

Colloid

A state of solid matter which is aggregated in very small particles, intermediate between molecular dimensions and normal crystals, with a size smaller than the wavelengths of visible light, and now preferably called **nanoparticles**. The term **colloid** tends to be reserved for 'gluey' substances, macromolecules such as gum, **gelatin**, **collodion** or **albumen**, used as binders in photographic materials.

Compound

The substance resulting from two or more elements entering into chemical combination.

Complex

A chemical compound formed from one or more **ligands** binding to a metal **cation**.

Complexing agent

Another name for a **ligand**. See **chelate**.

Concentration

In general, the amount of one substance dispersed within a perfectly **homogeneous** mixture. Most commonly, it applies to solutions in water or other liquids and can be measured in several different ways: %w/w; %w/v; %v/v; g/l; molarity (mol/dm^3).

Coordination number

The number of nearest neighbour atoms to the central atom or ion in a coordination compound, or in a crystal lattice.

Crystalline

A solid that has a regular repeating lattice structure of **atoms, molecules or ions**.

Cyanotype

A **siderotype** process invented by Sir John Herschel in 1842 in which the **photoproduct** from exposure of ammonium ferric citrate reacts with a ferricyanide to give Prussian blue, ferric ferrocyanide, which constitutes the image.

Deliquescence

Property of a solid having a tendency to absorb water from the atmosphere, and then to dissolve in it, to form a solution.

Density

The property of a substance expressed by its mass per unit volume. The usual units are g/cm³. See also **optical density**.

Density (optical)

Universally given the symbol D, and loosely referred to in photographic contexts simply as density, it is defined as the logarithm (to base 10) of the opacity:

$$D = \log_{10}(I_0/I_t) \text{ or } 10^D = I_0/I_t$$

where I_0 is the intensity of incident light and I_t is the intensity of light transmitted.

Optical densities of superimposed layers are additive, whereas transmittances and reflectances or opacities must be multiplied. Three conditions of measurement must be defined for optical density: the geometry of the light beam may be specular, diffuse or doubly diffuse; and the wavelength response of the photoreceptor may be spectral, visual (photoptic), printing, or arbitrary.

Density range

The difference in **optical density** between the lightest and darkest parts of an image.

Desiccant

An inexpensive substance that readily absorbs water from the atmosphere, such as anhydrous calcium chloride or silica gel. Used to create a dry chamber e.g. for the storage of sensitized but unexposed papers.

Developer

A chemical reagent used to treat an exposed photographic paper in order to bring out the final image in a stable substance.

Effervescence

The dignified word for 'fizzing' – to describe the evolution of a gas, as bubbles, from a liquid.

Electron

The fundamental particle of negative electricity.

Element

A fundamental constituent of matter that cannot be split into simpler constituents by chemical means (i.e. at low energies). Consisting of one type of **atom** only, with a characteristic **atomic number**.

ELISA

Antibody analysis

EPR

Electron Paramagnetic Resonance Spectrometry depends on the presence of unpaired electrons within the sample, which absorbs radio-frequency radiation when placed within a strong magnetic field. Iron compounds commonly have unpaired electrons and this can provide a sensitive technique for their detection and the characterization of the metal site.⁸³⁹

Equimolar

Having equal amounts or concentrations on the molar scale of two chemical components, i.e. equal numbers of molecules.

EXAFS or XAFS

Extended X-Ray Absorption Fine-structure Spectrometry can give information about the 'coordination sphere' of a particular element, *i.e.* the distances of the atoms that are directly bonded to it, and the nearest neighbours. This technique has recently been applied to the conservation problem of the state of the iron in the timbers of the Tudor flagship, *Mary Rose*.⁸⁴⁰ Another conservation application to iron compounds is the collaborative project on the pigment Prussian blue, between the Smithsonian Institute and the French synchrotron **SOLEIL**.⁸⁴¹

Exposure (photographic)

Intensity of light multiplied by the duration of the exposure.

Exposure = Illumination x time.

Usually given the symbol H, the basic units of exposure are lux seconds.

Exposure scale

The number of **stops** of exposure needed to transform a photographic material from the minimum **optical density** (usually white) of the paper base to the maximum density (black or other colour). It may also be expressed as a $\log_{10}(\text{Exposure})$ value, where a range of 0.3 = 1 stop, and the scale is additive.

Ferric/ferrous

The names given to the element iron when chemically combined in its two commonest **oxidation states** of +3 and +2, respectively: the **cations** Fe^{3+} and Fe^{2+} , now designated by iron(III) and iron(II).

Fluid ounce

An ambiguous obsolete unit of liquid volume: in the UK the British Fluid ounce was 28.412 cm^3 ; in the USA it was 29.573 cm^3 .

Formula (chemical)

The composition of a pure substance written in chemists' shorthand form using the symbols for the chemical **elements**, with their relative numbers of **atoms** in the molecule written as subscripts.

Formula weight

The sum of the **atomic weights** of all the **atoms** making up the **formula** of the substance; also known as **relative molecular mass**. In earlier texts generally referred to as the Molecular Weight.

FTIR

Fourier Transform Infra-Red Spectrometry can identify the functional groups present in molecular species, by their characteristic bond-stretching and angle-bending vibration frequencies which absorb radiation in the **infrared** region of the spectrum. It is especially effective for providing "fingerprints" of polar functional groups formed by the lighter elements, *i.e.* organic molecules, such as oxalates, and can be applied to the study of surfaces to identify coatings on paper.

GC-MS

Gas Chromatography and Mass Spectrometry provide a precise characterization of volatile (organic) species present in samples such as paper sizing or coating agents. **LC-MS** is similar in principle - but using liquid phase chromatography.

Gelatin

A very complex organic **macromolecular** material (a protein, or polypeptide, consisting of long chains of linked aminoacids) obtained from animal skins and bones (called ossein). Used as a **colloidal** binder in the preparation of photographic emulsions, and as a surface **sizing agent** for some papers. In the refining process, gelatines can be acidic or alkaline and oxidised or not.

Grain

An obsolete unit of weight seen only in old recipes. Abbreviation: gr. Avoid confusing it with grams, abbreviation g: 1 grain = 0.0648 grams.

Halides

The singly-charged **anions** - fluoride, chloride, bromide or iodide - of the group of elements known as the halogens: fluorine, chlorine, bromine or iodine, in combination with other elements; all metals form halides.

Hardening

Of **colloids** such as **gelatin** or gum: the process of rendering them insoluble in water - also resembles tanning.

Homogeneous

Uniform throughout, with no internal boundaries or surfaces - consisting of a single phase, either solid, liquid, or gas.

Humectant

A substance that tends to attract moisture. See **hygroscopic**.

Humidify

To take up water vapour from the atmosphere.

Hydrate

(verb) To allow to take up water, often from the vapour. To **humidify**.

(noun) A solid containing water of crystallization. An hydrated salt.

Hydration

The process of taking up or absorbing water.

Hydrogen ion

The ionised hydrogen **atom** H^+ . Since this is a bare **proton**, it will attach itself to the most available **molecule**, e.g. with water forming the hydronium ion H_3O^+ , or with ammonia forming the ammonium ion H_4N^+ .

Hydrolysis

Decomposition of a substance by water or **alkali** (OH^-). In the case of a metal **salt**, to give the metal hydroxide or (sometimes) oxide.

Hydrometer

A device for measuring the relative **density** (specific gravity) of liquids by means of the partial immersion of a calibrated float.

Hydrophilic

Having an affinity for water.

Hydrophobic

Having the property of repelling water.

Hygrometer

An instrument for measuring **relative humidity** (RH) in the air.

Hygroscopic

Having a tendency to absorb water from the atmosphere. Compare with **deliquescent**.

Hypo

An obsolete C19th name, still used by some photographers, which is short for "hyposulphite of soda" – the substance now called sodium thiosulphate. It is universally employed as a fixing agent in silver photography because of its ability to dissolve silver halides, a property discovered in 1819 by Sir John Herschel.

ICP-MS

Inductively coupled plasma mass spectrometry – elemental analysis.

IR

Infrared radiation; this is electromagnetic radiation having wavelengths just longer than visible light, i.e. ranging from 750 nm to about 1mm. Infrared radiation is responsible for radiant heat.

Ion

An **atom** or **molecule** that carries an electric charge, due to gain or loss of **electrons**. The charge is written superscripted following the chemical symbol, e.g. Fe^{3+} . See **anion** and **cation**.

Kallitype

A **siderotype** process invented by W.W.J. Nicol in 1889 in which the **photoproduct** from exposure of ferric oxalate reduces silver nitrate to give a silver image.

Kaolin

The rock composed chiefly of the soft white mineral kaolinite, known as china clay, which can be fired to make porcelain. Kaolinite is also employed as a filler in papermaking to provide a glossy surface. Chemically it is an **aluminosilicate**, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$.

Kelainotype

A **siderotype** process invented by Sir John Herschel in 1842 in which the **photoproduct** from exposure of ammonium ferric tartrate reduces mercuric chloride or nitrate to mercury metal, which constitutes the image, but which proves highly impermanent.

Laminar structure

Having a layered structure – particularly in the context of photographic prints on paper, which are characterised as having one, two or three layers.

Latent image

The initial effect of light on a crystal of silver halide, to produce a sensitivity speck consisting of a few atoms of silver, which renders the whole crystal reducible into a grain of silver metal by a suitable **developing agent**. The latent image is invisible to the naked eye.

Ligand

A **complexing agent**, i.e. any **molecule** or **ion** capable of binding chemically to a metal **cation** to give a molecular compound called a metal complex. E.g. chloride is the ligand in PtCl_4^{2-} .

Molarity

The **concentration** of a solution expressed as the number of **moles** of solute dissolved in one litre of the solution.

Molar ratio

The relative proportions of two substances expressed in terms of their respective numbers of **moles**, i.e. their relative numbers of **molecules**. It is then obvious why chemicals generally react or combine in simple proportions when expressed as molar ratios.

Mole

The chemist's unit to measure the amount of a pure substance. A mole of any substance is equal to the **formula weight** or **relative molecular mass** measured in grams. It is more fundamental than just weight or mass,

because one mole of any substance always contains the same number of **molecules** (called Avogadro's number = 6.022×10^{23}).

Molecular formula

The chemists shorthand designation to identify a pure substance, which gives the numbers of **atoms** of the different chemical **elements** combined within its **molecule**, and sometimes an indication of the way they are bonded together.

Molecular weight

Another name for **formula weight**. Now more correctly referred to as **relative molecular mass**.

Molecule

The smallest and simplest particle of a chemical substance or compound that can exist and still retain the identity of the whole. Molecules are composed of **atoms** chemically bonded in fixed proportions, and have definite 3-dimensional shapes.

Mössbauer Spectrometry

This type of nuclear γ -ray spectrometry is applicable to studying the nature of iron compounds, and yields information about their oxidation states and the symmetry of the local coordination environment. E.g. it provided the first proof of the exact chemical nature of Prussian blue: iron(III) hexacyanoferrate(II).

Nanometer (nm)

An SI unit of length: one billionth (10^{-9}) of a meter, convenient for measuring the wavelength of visible light, which approximately spans the region of the spectrum between 400 nm (violet) and 780 nm (deep red).

Nanoparticle

A particle of a substance having a size intermediate between that of atoms and the wavelength of visible light, i.e. in the region of 1 to 200 nm. See **colloid**.

Neutral

Neither **acid** nor **alkaline**. Neutrality prevails when the **hydrogen ions** and **hydroxide ions** in a water solution are equal in number. i.e. pure water is neutral, having **pH** 7.

Noble metal

Alchemical name for metals which are substantially unchanged by fire; i.e. metallic elements that resist oxidation, such as platinum palladium, gold and silver.

OCT

Optical Coherence Tomography

Oxalate

A **salt** containing the oxalate **anion**, $C_2O_4^{2-}$, derived from oxalic acid, $H_2C_2O_4$, which occurs naturally in rhubarb, sorrell and spinach.

Oxidation

The removal of **electrons** from an **atom** or **molecule**, in consequence of which it becomes more positively charged (or less negatively charged). An increase in the **oxidation state** of an atom or **ion**. Contrast with **reduction**.

Oxidation state

A formal electric charge that may be assigned to an **atom**, either free or in a **molecule**, which is calculated by the number of **electrons** it has effectively lost, compared with the neutral atom. Shared electrons are always formally allocated to the more electronegative of two bonded atoms. Conventionally, the oxidation state is written, in parentheses, in Roman numerals following the name or symbol of the element, e.g. iron(III), or Fe(III), and pronounced "iron-three".

Palladiotype

A **siderotype** process invented by William Willis in 1917 in which the **photoproduct** from exposure of ferric oxalate is made to reduce sodium tetrachloropalladate to give a palladium image.

Parchmentizing

A treatment for **cellulose** paper with strong sulphuric acid which renders it more translucent and rather brittle, resembling parchment. It destroys the regular structure of the fibres and renders the cellulose **amorphous**.

Periodic Table

A sequential arrangement of all the known **elements**, in order of increasing **atomic number**, in which elements having similar outer **electron** configurations, and therefore similar chemistry, are tabulated in the same vertical column called a Group. The number of Groups in each row of the Periodic Table is 2, 8, 8, 18, 18, 32, 32; each commencing with an alkali metal and terminating with an inert gas.

pH

A measure of the **acidity** or **alkalinity** of a solution. It is equal to the logarithm (to base 10) of the reciprocal of the **hydrogen ion molarity**:
 $\text{pH} = \log_{10} 1/[\text{H}^+]$ or $\text{pH} = -\log_{10}[\text{H}^+]$

Neutrality in water corresponds to pH 7; acidic solutions have smaller, and alkaline solutions greater pH than 7, with a range usually lying between 0 and 14. Every unit decrease in the pH represents a ten-fold increase in the acidity.

Photon

The fundamental particle of light, and of electromagnetic radiation in general.

Photoceramic

A photographic image formed upon, or transferred to, a ceramic substrate, and often fired under a glaze to render it highly permanent.

Photochemistry

The study of chemical changes brought about by the absorption of light.
See **actinic**.

Photoproduct

A substance produced by a **photochemical** reaction.

Photosensitizer

A substance capable of responding to light by undergoing some physical or chemical change.

Platinic/platinous

The names given to the element platinum when chemically combined in its two commonest **oxidation states** of +4 and +2, respectively, now designated by platinum(IV) and platinum(II).

Platinotype

A **siderotype** process invented by William Willis in 1873 in which the **photoproduct** from exposure of ferric oxalate is made, by an oxalate developer, to reduce potassium tetrachloroplatinate(II) to give a platinum image.

Precipitate

An insoluble solid thrown down in a solution due to a chemical reaction between the soluble components.

Printout process

A phenomenon in which the photographic image appears during the **exposure** due to the action of the light alone. Printout materials usually require a very heavy exposure, compared with those forming a **latent image** which is developed by chemical reaction after the exposure.

Proton

A fundamental positively-charged particle, the nucleus of the hydrogen **atom**, i.e. the **hydrogen ion**, H^+ . Its charge is equal, but opposite in sign, to that of the **electron**.

Raman Spectroscopy

Raman spectroscopy occurs in the modification of scattered light, usually in the visible region. It provides information on molecular vibration frequencies, and is often complementary to infrared spectrometry, because it is strongest in detecting highly polarizable groups formed by heavier atoms, and having lower vibration frequencies, *i.e.* inorganic complexes. It should be useful for detecting the presence of, for example, $[PtCl_4]^{2-}$ in unexposed specimens of Willis's Platinotype paper.

Reagent

A pure chemical, usually dissolved in a **solvent** (in solution) – often water – at a **concentration** suitable to perform a test or carry out a reaction.

Redox reaction

A **reduction-oxidation** reaction, involving the transfer of **electrons** from one **atom, molecule** or **ion**, to another.

Reduction

The addition of **electrons** to an atom or **molecule**, in consequence of which it becomes more negatively charged (or less positively charged). A decrease in the **oxidation state** of an atom or ion. Contrast with **oxidation**. The word 'reduction' is also used in photography to denote a process of diminishing the **optical density** of an image by dissolving away some of its substance. It is an unfortunate source of confusion that such a process is usually, chemically speaking, an **oxidation** (e.g. of silver metal).

RH

Relative Humidity. The ratio, defined as a percentage, of the amount of water vapor present in the atmosphere to the amount that would have been present if the same atmosphere were saturated (i.e. contained all the water-vapor it could hold) at that temperature.

RMM

Relative Molecular Mass. The sum of the relative atomic masses of all the **atoms** making up the **molecular formula** of the substance. Also called **molecular weight** or **formula weight**.

Salt

Any substance composed of **cations** and **anions**; i.e. an **ionic** compound. "Common salt" is sodium chloride: Na^+Cl^- . Salts result from the reactions of **acids** with **bases**.

Salted paper print

A print formed on paper sensitized with silver chloride, formed by first soaking in common salt solution (sodium chloride) *ca.* 2% *w/v*, drying, then brushing over with excess silver nitrate solution *ca.* 12% *w/v*.

Saturated solution

A solution that cannot contain any more **solute**, at a specified temperature. Marked by the presence of excess solid in contact with it.

SEM-EDX

Scanning Electron Microprobe with Energy Dispersive X-ray spectrometry. An analytical technique using an electron microscope's beam of electrons to excite the characteristic X-ray spectra of the **elements** present. The sample must be small (~cm) so it may be effectively a 'destructive' technique, but it is carried out in *vacuo*, so has the advantage over **XRF** that light elements can also be detected, and the area analysed can be imaged at high magnification.

Sensitizer

The solution (usually **aqueous**) of light-sensitive chemicals that is coated onto a paper (or other surface) to make a photographic printing material.

Sensitometry

The assessment of **photochemical** response in a photographic material, by **exposure** to a measured illumination for a given time, and then measurement of the **optical density** of the image formed, under specified processing conditions.

SERS

Surface-Enhanced Raman Spectroscopy – is a strengthening of the Raman intensity when the molecular species is adsorbed on the surface of metal nanoparticles, such as exist in photographic images. It has not yet been applied to photographs, but has potential for new information.

Siderotype

A collective name, originally due to Sir John Herschel, for all the **photochemical** printing methods based on a **photosensitive iron salt**.

Sizing agent

A glutinous preparation (usually of a **colloid** such as **gelatin** or starch) used to treat paper or fabric to diminish its absorbency. Some sizing agents, such as resins and Aquapel™ are **hydrophobic** (water-repellent).

Solar enlarger

An optical device using a large condensing lens to gather the sun's light to project the image of a negative via a second lens onto photographic papers of low sensitivity, such as **Platinotype**, for printmaking purposes. A tracking device is needed to follow the sun's apparent motion over the lengthy exposures.

Solarization

A photographic phenomenon in which increasing **exposure** diminishes the **optical density** of the image – also called reversal.

Solubility

The maximum weight of the substance that will dissolve completely in a given volume of **solvent** at a prescribed temperature. Usually given in units of g/100 cm³ of solution, or g/100 cm³ of solvent. N.B. these differ. The weight of substance needed to make 100 cm³ of **saturated solution**.

Solute

The substance which is dissolved in a **solvent** to make a **solution**.

Solution

A liquid which has another substance(s) dissolved in it. True solutions are always clear i.e. they do not perceptibly scatter light (though they may absorb it, i.e. be highly coloured). Contrast with a **suspension**.

Solvent

A liquid capable of dissolving other substances (solid, liquid or gaseous) to form **solutions**.

SQUID

Superconducting Quantum Interference Device for magnetometry. Again applicable to compounds with unpaired electrons, yielding magnetic moments, especially those of iron in which the magnetic centres may be interacting with one another – indicative of an oligomeric or polymeric structure.

Stop

In photography, one stop more is a doubling, and one stop less a halving of the **exposure**. The term is also used to describe differences in **optical density**: one stop = difference in optical density of 0.3. This corresponds to a doubling or halving of the **transmittance** or reflectance because $\log_{10}2 = 0.301$.

Surfactant

An agent that greatly reduces the surface tension of a liquid (usually water), enhancing its ability to wet objects, or penetrate the **cellulose** fibres of paper. E.g. Tween 20™.

Suspension

Small particles of an insoluble solid dispersed in a liquid or a gel.

Supersaturated

A solution, at a specified temperature, that contains more **solute** than is permitted by the equilibrium **solubility**. If scratched, jarred or 'seeded', it may rapidly crystallise or **precipitate**.

Transmittance

The fraction of the intensity of the incident light passing through an object.

Transmittance = Intensity of Transmitted light / Incident light = I_t/I_o

It is the reciprocal of the Opacity, I_o/I_t .

Transmittance is sometimes expressed as a percentage: $100 I_t/I_o \%$

UV

Ultraviolet radiation Electromagnetic radiation with wavelengths from 400 nm to about 50 nm. Conventional divisions of the ultraviolet spectrum are: UVA 400–315 nm; UVB 315–280 nm; UVC 280–200 nm.

The so-called 'near ultraviolet' UVA is the most suitable **actinic** radiation for **siderotype** processes.

UV-Visible spectroscopy

Ultra-Violet and Visible spectroscopy gives an indication of the electronic transitions occurring in molecular species; it is particularly significant for transition-metal complexes, e.g. the Ligand-to-Metal-Charge-Transfer absorption bands of iron(III), and can be applied to studying surfaces, as well as solutions.⁸⁴²

Vellum

Originally, a parchment made from the bleached and scraped skin of a calf, but in modern papemaking it denotes an entirely vegetable sheet in which

the cellulose paper pulp is heavily beaten to produce a translucent or even semi-transparent sheet: "tracing paper".

Weight of paper

A measure (thickness x density) of a paper sheet. Its units are weight per unit area: grams per square meter, g/m² (sometimes written as gsm). In the USA, paper weights are sometimes given in lbs (imperial pounds weight per ream of ca. 500 sheets) but this is an unspecified measure, which depends on the sheet size. For imperial-sized sheets (30 x 22 inches) the relationship is:

$$\text{Weight in gsm} = 2.13 \times \text{weight in lbs.}$$

XANES

X-Ray Absorption Near Edge Spectrometry is a cousin of **EXAFS**

XRF

X-Ray Fluorescence spectrometry. Non-destructive analytical technique to identify the heavier elements – usually of **atomic number** greater than 18 (argon) – present in a sample, unless a helium flush is used to displace the atmosphere in the intervening path between source and object. It does not identify the elements' state of chemical combination. The method as usually applied is only semi-quantitative.

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 - 22 Victor Fouque, *The Truth concerning the Invention of Photography: Nicéphore Niépce, his Life, Letters and Works*, Trans. Edward Epstean, New York: Tennant and Ward, 1935.
 - 23 Larry J. Schaaf, *Records of the Dawn of Photography: Talbot's Notebooks P & Q*, Cambridge University press, 1996, P125.
 - 24 Reports on Meetings of the Royal Society, *The Athenaeum*, No. 595, 23 March 1839, 233. See also: R. Derek Wood, "Fourteenth March 1839, Herschel's Key to Photography, the way the moment is preserved for the future." *Jubilee - 30 Years ESHPh. Congress of Photography in Vienna*, Anna Auer and Uwe Schögl (eds.), Fotohof edition nr.104, Salzburg, Austria: 2008, 18 - 31.

<http://www.midley.co.uk/articles/14march1839.htm>

http://www.midley.co.uk/sourcetexts/athenaeum_23mar1839_223.htm#herschel

- ²⁵ The reaction is a photoaquation and requires the presence of a substantial amount of water, which would have been difficult to achieve in a paper.
- ²⁶ Sir John F.W. Herschel, "On the Chemical Action of the Rays of the Solar Spectrum on Preparations of Silver and other Substances, both Metallic and non-metallic, and on some Photographic Processes", *Philosophical Transactions of the Royal Society*, **131**, 1840, 1–59.
- ²⁷ Mike Ware, *Cyanotype: the history, science and art of photographic printing in Prussian blue*, London: Science Museum and National Museum of Photography, Film & Television, 1999, 24–27, and references cited therein.
<http://www.mikeware.co.uk/mikeware/downloads.html>
See also: *idem*, "Herschel's Cyanotype: Invention or Discovery?" *History of Photography*, **22:4**, Winter 1998, 371–379.
- ²⁸ Sir John F.W. Herschel, "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*, **132**, 1842, 181–221.
- ²⁹ Sir John F.W. Herschel, "On Certain Improvements on Photographic Processes Described in a Former Communication, and on the Parathermic Rays of the Solar Spectrum", *Philosophical Transactions of the Royal Society*, **133**, 1843, 1–6.
- ³⁰ "Proceedings of Learned Societies: Royal Society, June 16 1842", *The London, Edinburgh and Dublin Philosophical Magazine and Journal of Science*, series 3, **21**, 1842, 227.
- ³¹ Sir David Brewster, (Ed.), "Drawing by the Agency of Light", *The Edinburgh Review*, **76:154**, January 1842, 339. The same article is reprinted in *The Penny Mechanic and Chemist*, No. 146 3rd series, 29 July 1843, 236–8. Brewster again uses the word in *The North British Review*, **7:14**, 1847, 474.
- ³² Henry Watts, *A Dictionary of Chemistry*, Vol. 5, London: Longmans, Green & Co., 1868, 240.
- ³³ Robert Hunt, *Researches on Light*, London: Longman, Brown, Green and Longmans, 1844; reprint edition 1973 by Arno Press Inc.
Hunt's chemistry deserves further investigation; he appears to have prepared potassium hexacyanatoplatinate(IV), or possibly hexacyanoplatinate(IV), which he found to be light sensitive, and 'developable' with mercury(I) nitrate, so it is likely that the evanescent images he obtained were constituted of mercury.
- ³⁴ http://www.edinphoto.org.uk/1_early/1_early_photography_-_photographers_burnett.htm
- ³⁵ *The Daily Scotsman*, Thursday, Sept. 22, 1859, 5, (1326), 2.

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- ³⁶ C.J. Burnett, 'On the Production of Direct Positives— on Printing by the Salts of the Uranic and Ferric Oxides, with Observations Climetic and Chemical', *The Liverpool and Manchester Photographic Journal*, **2**, 1858, 99, 111, 127, 155; *idem*, *The Photographic Journal* (Liverpool), **6**, 1859, 181, 185, 193; **7**, 1860, 55–6, 134–5.
- ³⁷ For an interesting review of Burnett's work see Ian Cottington, and references cited therein: Ian Cottington, "Platinum and Early Photography", *Platinum Metals Review*, **28**:4, 1984, 178–188; and in *History of Photography*, **10**:2, 1986, 131–139.
- ³⁸ C.J. Burnett, "On the application of Uranium and other matters to Photography", *Photographic Notes*, **2**, 1857, 97–101, 160–4, 181–4, 345–6; "Description of Mr. Burnett's Pictures in the Photographic Exhibition, Suffolk Street", *Journal of the Photographic Society*, 1859, 182–3.
- ³⁹ C.J. Burnett, "On the application of Uranium and other matters to Photography", *Photographic Notes*, **2**, 1857, 345–6.
- ⁴⁰ Abel Niépce de Saint-Victor, "On a New Action of Light", *Photographic Notes*, **3**, 1858, 85–8.
- ⁴¹ J. Wothly, "New Printing Process with Urano-Platinum Collodion", *Humphrey's Journal*, 10 August, 1866.
- ⁴² Mike Ware, *Gold in Photography: the History and Art of Chrysotype*, Brighton: ffotofilm publishing, 2006.
- ⁴³ Ernest de Carranza, "Procédé de tirage des positives par le chlorure de platine", *Bulletin de la Société Française de Photographie*, **15**, April 1856, 82–84; *La Lumière*, **6**:8, 23 February 1856, 29; translated in *Journal of the Photographic Society*, **3**:40, 21 March 1856, 14; see also: H.L.T. Haakman, "Toning paper positives with platinum", *The Photographic News*, **1**, 28 January 1859, 251; **2**, 1859, 204, 263.
- ⁴⁴ D. Stulik, H. Khanjian, A. de Tagle, and A. Bothelo, "Investigation of Jean-Louis-Marie-Eugene Durieu's toning and varnishing experiments: a non-destructive approach", *ICOM-CC Preprints of the 3rd Triennial Meeting, Rio de Janeiro*, September 2002, London: James and James, 658–663.
- ⁴⁵ *Photographic News*, **3**, 1859, 38. At this time, "platinic chloride" was thought to be a bichloride, rather than the tetrachloride as we now understand.
- ⁴⁶ Lyonel Clark, *Platinum Toning*, Amateur Photographer's Library No. 1, London: Hazell, Watson, & Viney, Limited, 1895 (4th Edn.).
- ⁴⁷ British patent no. 2,800, November 11, 1864. An example of Willis senior's 'aniline' reprographic process is in the National Media Museum, Bradford: a copy of an architectural plan of "Smallwood Manor", inaccurately labelled as "The first platinum print by Willis". See: Dr. Dusan Stulik and Art Kaplan,

Alternative Process Photography and Science meet at the Getty, Getty Conservation Institute, 2010, 6–7

- ⁴⁸ Vincent Robert Alfred Brooks (1815–1885). See:
https://en.wikipedia.org/wiki/Vincent_Brooks,_Day_&_Son
- ⁴⁹ The church spire is characteristic and the chimney belongs to the pumping station of the local waterworks. See:
https://en.wikipedia.org/wiki/St_Mary_Cray
<http://hidden-london.com/gazetteer/st-mary-cray/>
http://orpington-history.org/articles_all/article_1.htm
- ⁵⁰ See the autobiography of F. Vincent Brookes at:
<http://vincentbrooks.blogspot.co.uk/>
- ⁵¹ I am indebted to Shannon Perich of the NMAH for bringing this fascinating photograph to my attention. For the historical background to this acquisition see: Helena E. Wright. "Prints at the Smithsonian: The Origins of a National Collection." Washington DC: NMAH, 1996. Idem, "The Osborne Collection: Photomechanical Incunabula." *History of Photography*, 24 (Spring 2000), 42–46.
- ⁵² An Alfred Clements is listed in the *Register of Births* for January 1846 in the Malling District of Kent.
- ⁵³ William Willis, "Photographic process for Copying Drawings", US Patent No. 55,592, 12 June 1866.
<http://www.google.co.uk/patents/US55592>
- ⁵⁴ In American usage, a "shop" is a workshop. The American for an actual shop is a "store". The American for an actual store is a "depository".
- ⁵⁵ Helena E. Wright. "Photography in the printing press: the photomechanical revolution."
<http://www.artefactsconsortium.org/Publications/PDFfiles/Vol4Pics/4.02.Pictures-Wright,Photography75ppiWEBF.pdf>
- ⁵⁶ "Alfred Clements and his work." *The Photographic Times*, 27 (October 1895), 216.
- ⁵⁷ Census returns describe his occupation as Merchant's Warehouseman, then Bank Clerk.
- ⁵⁸ Mike Ware, "The Eighth Metal: The Rise of the Platinotype Process", in *Photography 1900: The Edinburgh Symposium*, Julie Lawson, Ray McKenzie, and Alison Morrison-Low (Eds.), Edinburgh: National Museums of Scotland and National Galleries of Scotland, 1994, 99–111.
http://www.mikeware.co.uk/mikeware/Eighth_Metal.html

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- ⁵⁹ So-called because it was also capable of dissolving the 'royal' metal, gold.
- ⁶⁰ In the interests of readability, the chemical nomenclature is somewhat simplified here; platinic chloride, now known as platinum(IV) chloride, PtCl_4 , is usually obtained from this reaction in the form of a complex acid: hydrogen hexachloroplatinate(IV) hexahydrate, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$.
- ⁶¹ Mr. W. Willis, "A Recent Improvement in the Platinotype Process", *The Journal of the Camera Club*, 2:17, 1888, 47–51; 2:19, 1888, 99; 2:20, 1888, 103.
- ⁶² 'Platinous' salts are of divalent platinum(II); 'platinic' salts are of tetravalent platinum(IV). The latter oxidation state was thought erroneously to be divalent, and the former monovalent, until quite late in the C19th. Thus, in Thomas Sutton and George Dawson (eds.), *A Dictionary of Photography*, London: Sampson Low, Son & Marston, 1867, platinic chloride is described as "bichloride of platinum", formula PtCl_2 . The same *Dictionary* by 1895 calls it "platinum perchloride", and has the formula correct, as $\text{PtCl}_4 \cdot 2\text{HCl} \cdot 6\text{H}_2\text{O}$.
- ⁶³ Also called platinum(II) chloride, PtCl_2
- ⁶⁴ H.G. Magnus, *Poggendorff's Annalen*, 14, 1828, 241.
- ⁶⁵ Mr. W. Willis, *loc. cit.*, Ref 61.
- ⁶⁶ In contemporary nomenclature: potassium tetrachloroplatinate(II), K_2PtCl_4
- ⁶⁷ Chapman Jones, *The Science and Practice of Photography*, London: Iliffe, 1904, 441.
- ⁶⁸ e.g. Blomstrand (1871), Thomsen (1877), Knoefoed (1888), Lea (1894), Kurnakoff (1894), Pigeon (1895), Grîger (1897), Wolfram (1900), Klason (1904), Wohler and Frey (1909). For further details see J.W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, London: Longmans, Green and Co.
- ⁶⁹ J.W. Döbereiner, "Chemische Thätigkeit des Lichts und Erzeugung des (neutralen) Humboldtits auf Chemischem Wege", *Schweigger's Jahrbuch*, 62, 1831, 86, 90–96.
- ⁷⁰ Mike Ware, *Gold in Photography: the History and Art of Chrysotype*, Brighton: ffotofilm publishing, 2006, 56. There is also a translation in the Notes to: Robert Hunt, *The Poetry of Science, or Studies of the Physical Phenomena of Nature*, London: Reeve, Benham, and Reeve, 1849, 440.
- ⁷¹ This omission by Herschel is discussed in: Mike Ware, *Cyanotype: the history, science and art of photographic printing in Prussian blue*, London: Science Museum, 1999, 29–31.
- ⁷² Robert Hunt, *Researches on Light*, London: Longman, Brown, Green and Longmans, 1844, 147.
- ⁷³ Mr. W. Willis, *loc. cit.*, Ref 61.

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- ⁷⁴ Christie's, South Kensington, "19th and 20th Century Photographs", *Auction Catalogue*, 21st April 1988, Lot 110.
- ⁷⁵ Matthew Clarke, National Gallery of Art, *private communication*, 2015.
- ⁷⁶ Editorial, "A New Printing Process", *The British Journal of Photography*, **21**:717, 30 January 1874, 47, 49.
- ⁷⁷ Dr. Thomas Rodger, "On Platinotype", *The British Journal of Photography*, **24**, 13 April 1877, 172–3.
- ⁷⁸ Dr. Dusan Stulik and Art Kaplan, *Alternative Process Photography and Science meet at the Getty*, The Getty Conservation Institute, 2010.
http://www.getty.edu/conservation/our_projects/science/photocon/alt_processes.pdf
- ⁷⁹ William Willis, *British Patents*:
Improvements in Photo-chemical Printing, no. 2,011, 5 June 1873;
An Improved Process of Photo-chemical Printing, no. 2,800, 12 July 1878;
Improved Materials and Processes for Photo-chemical Printing, no. 1,117, 15 March 1880;
Improvements relating to Photo-chemical Printing, no. 1,681, 2 Feb. 1887;
Improvements relating to Photo-chemical Printing, no. 16,003, 21 Nov. 1887;
Improvements in or relating to Photographic Printing and Paper therefor, no. 20,022, 4 September 1913.
- ⁸⁰ Luis Nadeau, *History and Practice of Platinum Printing*, 3rd edn. New Brunswick: Atelier Luis Nadeau, 1994. This text also reproduces five of Willis's six patents.
- ⁸¹ All six patents have been transcribed by platinotype photographer Ian Leake, in his book, *The Platinum Printing Workshop*, second edition 2015, 155–166.
- ⁸² National Media Museum, photographic archive. I am indebted to Dr. Roger Taylor for much valuable information on the history of this aspect of photography.
- ⁸³ William Willis, "A New Process of Photo-chemical Printing in Metallic Platinum", *The British Journal of Photography*, **25**, 23 August 1878, 400;
idem, "Notes on the Platinotype Process", *The British Journal of Photography*, **26**, 14 February 1879, 73–4.
- ⁸⁴ "19th and 20th Century Photographs", *Auction Catalogue*, Christie's, South Kensington, London, 1988, item 107, 38.
- ⁸⁵ William Mansfield worked as a chemist for the Platinotype Company.
- ⁸⁶ W. Willis, Jun., "A New Process of Photo-Chemical Printing in Metallic Platinum", *The British Journal of Photography*, **25**, 23 August 1878, 400.
- ⁸⁷ W. Willis, Jun., "Notes on the Platinotype Process", *The Photographic Journal*, New Series **3**:3, 13 December 1878, 32–34. (Old series vol. no. 19).

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- ⁸⁸ W. Willis, Jun., "Notes on the Platinotype Process", *The British Journal of Photography*, **25**, 20 December 1878, 605–8.
- ⁸⁹ Helmut and Alison Gernsheim, *The History of Photography*, Oxford: University Press, 1955; London: Thames & Hudson, 1969.
- ⁹⁰ See letter from Charles Robinson of the Platinotype Co., to Ned Scott:
<http://www.thenedscottarchive.com/technical/platinotype.html>
I thank curator Norman Scott for making a copy of this letter available.
- ⁹¹ The collection of the Museum of the History of Science in Oxford has several tins of Platinotype paper; see Inventory nos. 60172 and 92955, whose lids state: "The Platinotype Company Ltd., Established 1878, Penge, London S.E."
- ⁹² James Young, "The Platinotype Printing Process", *The British Journal of Photography*, **27**, 16 January 1880, 29–30.
- ⁹³ From 1879 to 1881 the Company's first address was: 2 St. Mildred's Terrace, Bromley Road, Lee, Kent. In 1883 it transferred to 29 Southampton Row, High Holborn, London, until February 1884, when it moved to Charlotte Street, Bedford Square, London, and finally in 1903 to 22 Bloomsbury Street, New Oxford Street, London WC until 1914. Thereafter, the Company used only the Penge address that follows.
- ⁹⁴ At 66 Beckenham Road, Penge, later to become 66 High Street, Penge, London SE 20.
- ⁹⁵ One shilling 1/- = 12 d 'old' pence = 5 p 'decimal' pence = £0.05
- ⁹⁶ The earliest published mention that sensitized paper could be purchased seems to be by John Nicol, "A Plea for Permanent Printing", *The British Journal of Photography*, **26**, 18 July 1879, 339–340.
- ⁹⁷ The Platinotype Company, "The Platinotype Process", *The British Journal of Photography*, **26**, 26 September 1879,
- ⁹⁸ *The Photographic Journal*, 4 October 1879, 9;
http://erps.dmu.ac.uk/simple_finds.php?search=Platinotype&worp=p&submit=Search
http://erps.dmu.ac.uk/catalogue_single.php?h=ca2&pnum=E79A009&page=p&efn=W.+Willis%2C+Junr
- ⁹⁹ *The British Journal of Photography*, **26**, 24 October 1879, 505.
- ¹⁰⁰ "Royal Cornwall Polytechnic Society", *The British Journal of Photography*, **26**, 12 September 1879, 438.
- ¹⁰¹ W. Willis, Jun., "On some recent Improvements in Platinotype Printing, and on the use of the Electric Light in producing Direct Enlargements", *The British Journal of Photography*, **27**, 14 May 1880, 232–3.

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- ¹⁰² John Spiller, "The Fading of Platinotype Prints", *Journal of the Photographic Society of Great Britain*, 3, 1880, 74.
- ¹⁰³ George Dawson, "The Platinotype Printing Process", *The British Journal of Photography*, 27, 20 August 1880, 399–400.
- ¹⁰⁴ Editorial, "Prints by the Platinotype Process", *The British Journal of Photography*, 27, 16 July 1880, 345–6.
- ¹⁰⁵ From advertisements in: Capt. W. de W. Abney, *Photography with Emulsions*, London: Piper & Carter, 1885.
- ¹⁰⁶ James Young, "The Platinotype Printing Process", *The British Journal of Photography*, 27, 16 January 1880, 29–30.
- ¹⁰⁷ Henry Baden Pritchard, *The Photographic Studios of Europe*, London: Piper & Carter, 1882, 76–80.
- ¹⁰⁸ 5/- = £0.25. A significant sum at the time, equivalent to ca. £20 today, see: <http://www.measuringworth.com/ukcompare/>
- ¹⁰⁹ *The Amateur Photographer*, 11 July 1888, 27.
- ¹¹⁰ Mr. W. Willis, "A Recent Improvement in the Platinotype Process", *The Journal of the Camera Club*, 2:17, 1888, 47–50; *ibid.*, 2:19, 1888, 99; 2:20, 1888, 103; 4, 1890, 121.
- ¹¹¹ Mr. W. Willis, "A Recent Improvement in the Platinotype Process", *The Journal of the Camera Club*, 2:17, 1888, 47–50.
- ¹¹² Josiah T. Chapman, *Platinotype: simple instructions for working the process lately perfected, and now known as the Cold Development Method*, Manchester: John Heywood, August 1892.
- ¹¹³ Mr. W. Willis, "Recent Improvements in Platinotype", *The Journal of the Camera Club*, 6:69, 1892, 53–55.
- ¹¹⁴ John William Willis Clemes, *private letter to the author*, 28 October 1988.
- ¹¹⁵ W.H. Smith, "The New Platinotype Paper", *The British Journal Photographic Almanac and Photographer's Daily Companion*, 1893, 722–3.
- ¹¹⁶ "Photographic Society Committee on Positive Printing", *Journal of the Photographic Society*, 2, 21 May 1855, 160.
- ¹¹⁷ P.H. Delamotte, H.W. Diamond, T.F. Hardwich, T.A. Malone, J. Percy, H. Pollock, G. Shadbolt, *Journal of the Photographic Society*, 2, 1855, 251.
- ¹¹⁸ Advertisements, *The Year-Book of Photography and Photographic News Almanac*, 1898, vi.
- ¹¹⁹ Leon Vidal, "Platinotype Process", *The British Journal of Photography*, 33:1391, December 1886, 829–830.
- ¹²⁰ W.K. Burton, *Practical Guide to Photographic and Photomechanical Printing*, London: Marion & Co., 1892.

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- ¹²¹ John Nicol, "A Plea for Permanent Printing", *The British Journal of Photography*, **26**, July 18 1879, 339–340.
- ¹²² *The London Gazette*, 8 November 1889, 5938.
- ¹²³ Herbert B. Berkeley, "The Platinotype Process", *The British Journal of Photography*, **28**, 11 February 1881, 64–5.
- ¹²⁴ A. Horsley Hinton, *Platinotype Printing*, London: Hazell, Watson & Viney, Ltd., 1897, 7–8.
- ¹²⁵ Clara von Waldthausen, "Coatings on Salted Paper, Albumen, and Platinum Prints", in Constance McCabe (Ed.), *Coatings on Photographs: Materials, Techniques, and Conservation*, Washington DC: American Institute for Conservation, 2005, 79–95.
- ¹²⁶ W.J. Warren, *A Handbook of the Platinotype Process of Photographic Printing*, London: Iliffe, Sons & Sturmey Ltd., n.d., ca. 1899, 77–79.
- ¹²⁷ Percy Lund, *Photography for Novices*, London: W. Butcher & Sons, 1902, 3rd edition.
- ¹²⁸ In Sterling, 6 old pence are equivalent to 2.5 new pence, £0.025. This is equivalent to about £2.30 today, based on the Retail Price Index.
- ¹²⁹ Thomas Bolas, "Platinum and its Photographic Uses", *The Amateur Photographer and Photographic News*, 22 April, 1912, 410.
- ¹³⁰ "Visit to the works of the Platinotype Company", *The British Journal of Photography*, **58**, 2 June 1911, 416–7. A transatlantic account appears in: "What every photographer should know", *Wilson's Photographic Magazine*, **48**:655, July 1911, 325:
<http://archive.org/stream/wilsonsphotogra01yorkgoog#page/n349/mode/2up/search/325>
 This article is apparently derived from one in the *Amateur Photographer*.
- ¹³¹ "Croydon Camera Club", *The British Journal of Photography*, **58**, 17 November 1911, 884.
- ¹³² 'Our Roving Commissioner', "The Home of "Satista" and some New Developments", *The Photographic Dealer*, **29**, March 1915, 106–108. I thank Lee Ann Daffner for discovering this reference.
- ¹³³ Brian Coe and Mark Haworth-Booth, *A Guide to Early Photographic Processes*, London: The Victoria and Albert Museum, 1983, 80.
- ¹³⁴ Mr. W. Willis, "Platinotype – some new points", *The Journal of the Camera Club*, **7**: , 1893, 170–173.
- ¹³⁵ Mr. W. Willis, "Recent Improvements in Platinotype", *The Journal of the Camera Club*, **6**:69, 1892, 53–55.
- ¹³⁶ Mr. W. Willis, *loc. cit.* Ref. 135.
- ¹³⁷ Mr. W. Willis, *loc. cit.* Ref. 135.

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- ¹³⁸ W.H. Smith, "Modifications in Platinotype Produced by Variations in Strength and Temperature of Developer", *The Photographic Journal*, January 1911, 2–12.
- ¹³⁹ W.H. Smith, *loc.cit.* Ref. 138.
- ¹⁴⁰ F.C. Lambert, "Practical Points in Platinotype", *The Photographic Times*, **43:6**, June 1911, 222–225.
- ¹⁴¹ W.H. Smith, "Satista and Other Platinotype papers", *The Photographic Journal*, December 1915, 282–286.
- ¹⁴² Paul. L. Anderson, *Pictorial Photography: Its Principles and Practice*, Philadelphia: J.B. Lippincott Company, January 1917, 150 – 151.
- ¹⁴³ E.J. Wall and Franklin I. Jordan, *Photographic Facts and Formulas*, Revised Edn. by John S. Carroll, New York, Amphoto, 1975, 290.
- ¹⁴⁴ For a biographical note on Alfred Clements, see:
<http://photoseed.com/collection/single/eastward-at-sundown/>
- ¹⁴⁵ See Ref.144
- ¹⁴⁶ Initially at 17 East 17th Street, NY.
- ¹⁴⁷ H.A. Webb, "Willis's Platinum Process", *The Philadelphia Photographer*, **16:191**, November 1879, 328.
- ¹⁴⁸ Editor, "Willis's Platinum Printing Process", *The Philadelphia Photographer*, **16:190**, October 1879, 190.
- ¹⁴⁹ See advertisement in *The Philadelphia Photographer*, **17:203**, November 1880, 1.
- ¹⁵⁰ Then at 123 West 26th Street. See *The Photographic Times*, **27**, October 1895, 216.
- ¹⁵¹ *The Philadelphia Photographer*, **18:213**, August 1881, 256.
<http://archive.org/stream/philadelphiaphot1881phil#page/n5/mode/2up>
- ¹⁵² *The Philadelphia Photographer*, **19:217**, January 1882, 34.
<https://archive.org/details/philadelphiaphot1882phil>
see also:
The Photographic Times and American Photographer, **11**, November 1881, 436, 466, where the process is misspelt "plantinotype"!
- ¹⁵³ William Willis, jnr., "The Platinotype Process", *The Philadelphia Photographer*, **18:207**, March 1881, 85–87.
- ¹⁵⁴ Willis & Clements, *The Platinotype (patented)*, 2nd edn., Philadelphia: Chambers Printing House, 1885.
- ¹⁵⁵ *Instructions for Working the Platinotype Process*, 6th edn., London: The Platinotype Company, January 1883.

- ¹⁵⁶ *The Philadelphia Photographer*, 2:280, 21 August 1886, 510. See: <http://www.us.archive.org/details/philadelphiaphot18862phil>
- ¹⁵⁷ This year was originally inferred from the plea entered in 1913 by Alfred Clements regarding Tariff Schedules, in *Hearings before the Committee on Ways and Means, House of Representatives*, Volume 5. Washington: Government Printing Office, 1913:
- January 18 1913. " For 25 years we have imported a photographic paper from England known in the trade as "platinotype paper."
- Subsequent searches of the American photographic journals of 1888 confirmed this date.
- ¹⁵⁸ *The Philadelphia Photographer*, 18:207, March 1881, 80.
- ¹⁵⁹ *The Philadelphia Photographer*, 25:334, 17 November 1888, xv. <http://archive.org/stream/philadelphiaphot18882phil#page/n689/mode/2up>
- ¹⁶⁰ Alfred Clements, "Platinotype Processes", *Pacific Coast Photographer*, 1893, 299–300.
- ¹⁶¹ Alfred Clements, "Sepia Platinotype", *Camera Craft*, 12, 1906, 9–11. <https://babel.hathitrust.org/cgi/pt?id=mdp.39015075026578;view=1up;seq=19>
- ¹⁶² *The Platinotype: Simplest Photographic Process*, Philadelphia: Willis & Clements, 1908. I thank Constance McCabe for bringing this instruction booklet to my notice.
- ¹⁶³ Willis & Clements, "The Platinotype", Philadelphia: Willis & Clements, 1908.
- ¹⁶⁴ Carles S. Ogilvie, "Japine Sepia Platinotype", *Camera Craft*, 13:6, December 1906, 473–476.
- ¹⁶⁵ *Illustrated Philadelphia: Its Wealth and Industries*, New York: American Publishing and Engraving Co., 1889. See: <http://archive.org/stream/illustratedphila00amer#page/n3/mode/2up> for Platinotype enlargements by Mr. H.C. Bridle, see p.149; by Samuel W. Brown, see p. 203; and by Messrs Hodge & Huston, see p.269.
- ¹⁶⁶ Over the years, as inferred from published advertisements, instruction booklets, and Alf Parker's Scrapbook, Willis & Clements did business from at least ten different addresses in Philadelphia:
- | | |
|-----------|----------------------|
| 1881 | 631 Arch Street |
| 1885 | 23 North Seventh St. |
| 1886 | 1112 Hunter St. |
| 1888 | 912 Arch St. |
| 1889 | 913 Arch St. |
| 1890–1893 | 39 South Tenth St. |
| 1894–1904 | 1624 Chestnut St. |

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- 1905–1916 1814 Chestnut St.
1917 713 Walnut St.
1917–1924 604 Arch St.
1928 713 Walnut St.
- ¹⁶⁷ William Willis, "On some recent improvements in platinotype printing, and on the use of the electric light in producing direct enlargements", *The British Journal of Photography*, **27**, 1880, 232–3.
- ¹⁶⁸ *The Photographic Journal*, 4 October 1884, xxxiii. See Nadeau *History and Practice of Platinum Printing*, 3rd edn., 1994, 108.
- ¹⁶⁹ "Croydon Camera Club", *The British Journal of Photography*, **58**, 17 November 1911, 884.
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And as silently steal away."
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http://en.wikipedia.org/wiki/Solubility_table

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<http://www.mikeware.co.uk/mikeware/preparations.html>

A short video is at:

<https://dl.dropbox.com/u/47727259/coating.mov>

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