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46 Mike Ware, "The Technical History and Chemistry of Platinum and Palladium Printing" in *Platinum and Palladium Photographs: Technical History, Connoisseurship, and Preservation*, ed. Constance McCabe (Washington, D.C.: American Institute for Conservation of Historic and Artistic Works, 2017), 46–83.

# The Technical History and Chemistry of Platinum and Palladium Printing

# Mike Ware

Nothing is easier to see than what was found yesterday, and nothing more difficult than what will be found tomorrow. — Jean-Baptiste Biot

The reader will by now appreciate that this volume is richly embellished with illustrations of platinum photographs, in which one of the rarest and most stable of noble metals is subtly bound into cellulose, the commonest of nature's organic substances. This elegant paper printing process did not arise by chance: its development was largely the life's work of one man, William Willis Jr. (1841–1923), informed by the science of chemistry and spurred on by his concern to overcome the vulnerability of early photographs. Willis was not himself a photographer, but we should honor him as one of the first—and most influential—contributors to the conservation of photographs. His dedicated lifetime of research has ensured that the art of photography, as we have seen in the previous essay, is endowed with a legacy of the most permanent and beautiful images (fig. 1).

In contrast, however, the aim of the present essay is to expose the technical details of the archival process of Platinotype, which soon gained the summit of practice in the entire range of photographic art. The author hopes that this exposition is couched in language acceptable to readers steeped in the arts and humanities, while at the same time providing sufficient technical underpinnings and sources of reference for research by those pursuing a deeper understanding of the chemical science of Platinotype. To appreciate the historical context of this remarkable innovation we must now begin by returning to the dawn of photography itself.

#### Sir John Herschel's Siderotypes

The invention of photography in silver was first announced in January 1839 by Louis Jacques Mandé Daguerre and independently by William Henry Fox Talbot. Sir John Herschel, Talbot's colleague in the Royal Society, quickly took up research on photographic processes but soon found that silver chloride as an imaging substance could exhibit "capricious differences." He expressed his dissatisfaction with the comment, "I was on the point of abandoning the use of silver in the enquiry altogether and having recourse to Gold or Platina."<sup>1</sup> Here Herschel is recalling his discovery of 1831 that a particular platinum salt solution is sensitive to light, forming a white precipitate of "platinate of lime" when illuminated.<sup>2</sup> This aqueous photochemical reaction did not suggest itself to Herschel at the time as a possible photographic process because it cannot produce actual images. Nonetheless, platinum salts evidently remained in his mind:<sup>3</sup> Herschel's paper of 1840 to the Royal Society on his early photographic researches<sup>4</sup> reported a test of platinic chloride that, disappointingly, proved insensitive to light.<sup>5</sup>

In 1842, as part of his quest for a system of color photography, Herschel began experimenting with an iron salt, ammonium ferric citrate, which had been suggested to him by the young physician Dr. Alfred Smee.<sup>6</sup> This compound proved to be highly sensitive to light, which transforms it into a ferrous salt by a reduction-oxidation reaction that we might today represent by the equation:<sup>7</sup>

Figure 1. *Left*: William Willis Jr., the first silver-free platinum print, March 17, 1878, 21.6  $\times$  7.3 cm. The Metropolitan Museum of Art, Gilman Collection, Purchase, The Horace W. Goldsmith Foundation Gift, through Joyce and Robert Menschel, 2005, 2005.100.966.

*Right*: Verso, with inscription: "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."

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2b





Figure 2. Examples of Sir John Herschel's siderotype processes, 1842. 2a. Sir John Herschel, cyanotype

print,  $10.7 \times 7.9$  cm. From the c. 1838 engraving by H. Cook, *Still in My Teens* (from a painting by H. Richter). Harry Ransom Center, The University of Texas at Austin.

2b. Sir John Herschel, chrysotype print,  $10.4 \times 7.8$  cm. From the c. 1837 engraving by P. Lightfoot, *Rosolia* (from a painting by A. Penley). Harry Ransom Center, The University of Texas at Austin.

2c. Sir John Herschel, argentotype print,  $10.4 \times 7.8$  cm. From the c. 1836 engraving by Charles Rolls, *The Honourable Mrs. Leicester Stanhope* (from a painting by F. Stone). Harry Ransom Center, The University of Texas at Austin.

2d. Sir John Herschel, kelainotype print (with no discernible image), 10.7  $\times$  7.9 cm. From the c. 1838 engraving by H. Cook, *Still in My Teens* (from a painting by H. Richter). Harry Ransom Center, The University of Texas at Austin. Herschel's annotation on verso: "758."

One way of making a permanent image from this is to react the resulting ferrous ion with potassium ferricyanide to form the pigment Prussian blue—ferric ferrocyanide— with which Herschel printed blue photographic images that he named as cyanotypes:<sup>8</sup>

ferrous salt + potassium ferricyanide  $\rightarrow$  ferric ferrocyanide (Prussian blue) Fe<sup>2+</sup> + K<sub>3</sub>Fe(CN)<sub>6</sub>  $\rightarrow$  KFe[Fe(CN)<sub>6</sub>] + 2K<sup>+</sup>

Herschel's chemical intuition quickly suggested that the ferrous photoproduct should also reduce noble metal salts, i.e., silver nitrate to silver, or mercuric chloride to mercury, or gold chloride to gold, for instance, by the reaction:

> ferrous salt + gold chloride  $\rightarrow$  ferric salt + gold metal precipitate 3Fe<sup>2+</sup> + AuCl<sub>4</sub><sup>-</sup>  $\rightarrow$  3Fe<sup>3+</sup> + 4Cl<sup>-</sup> + Au $\downarrow$

but the analogous chemistry does not work for platinic chloride.

Thus Herschel successfully used ammonium ferric citrate in 1842 to print images photographically on paper, in Prussian blue, gold, silver, and mercury, so giving rise to the four new printing processes that he named respectively: cyanotype, chrysotype, argentotype, and kelainotype, which are exemplified in figure 2.<sup>9</sup> Herschel named all

<sup>48</sup> Mike Ware, "The Technical History and Chemistry of Platinum and Palladium Printing" in Platinum and Palladium Photographs: Technical History, Connoisseurship, and Preservation, ed. Constance McCabe (Washington, D.C.: American Institute for Conservation of Historic and Artistic Works, 2017), 46–83.

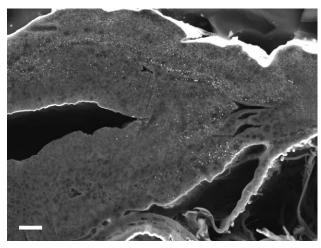


Figure 3. Electron micrograph of a cross section of a modern platinum-palladium print, 2013. Courtesy of Natasha Erdman, JEOL, and Patrick Ravines, SUNY, Buffalo State. Nanoparticles of image metal appear as white dots embedded in the upper walls of the cellulose fiber. Scale bar = 1 µm. such photographs based on light-sensitive salts of iron as "siderotypes," from the Greek word for iron, σιδηρος (*sideros*).<sup>10</sup> This neologism serves as a useful collective noun for the whole class of photographic processes within which the yet-to-be-invented platinotype and palladiotype would later find their context, as indicated in table 1.

The aesthetics of Platinotype's "subtle beauty" described in Andrea Nelson's essay may now be complemented with a physico-chemical view of the special qualities that all these siderotype photographs have in common and share with the salted paper print, emphasizing their differences from the popular albumen and gelatin silver prints of the historical mainstream of photography:

- The sensitizer is an aqueous solution absorbed into the surface cellulose fibers of the paper sheet: there is no colloidal binder layer, such as the albumen, collodion, or gelatin needed to hold in suspension the solid particles constituting silver halide "emulsions."
- The "single layer print" of fine, plain paper has great physical integrity because it cannot delaminate. It usually presents a perfectly matte surface that is immune to reflective glare under any lighting, but possesses a lively tactile finish, akin to those other works of art on paper—graphite drawings, etchings, engravings, mezzotints, and watercolors.
- The image substance of platinum or palladium nanoparticles is embedded within the surface fibers of the sheet (fig. 3). It confers on the image a subtly nuanced neutral gray—or sometimes sepia—tonal scale, which cannot be erased without removing the fibers themselves.
- The effect of light exposure is not "amplified" by chemical development of a latent image of the kind formed within silver halide crystals, so to ensure enough throughput of light, printing is usually done by contact, requiring a same-size negative.
- The siderotype processes are sensitive only to ultraviolet and blue light, so no darkroom is required; subdued tungsten illumination is safe for all manipulations.
- Archivally permanent images can be achieved with gold, platinum, and palladium, which do not suffer from the same vulnerability as silver.

As always, there are exceptions to some of these generalizations, which will be described below (and in the subsequent essays and technical highlights) and have been indicated here by the qualifier "usually."

Year	Inventor	Process Name	Image Substance
1842	Sir John Herschel	Cyanotype	Prussian blue
1842	Sir John Herschel	Argentotype	Silver
1842	Sir John Herschel	Chrysotype	Gold
1842	Sir John Herschel	Kelainotype	Mercury
1859	Alphonse Louis Poitevin	Ferrogallate	Iron gall ink
1872	William Willis Jr.	Platinotype	Platinum
1889	W. W. J. Nicol	Kallitype	Silver
1889	Arndt & Troost	Van Dyck	Silver
1917	William Willis Jr.	Palladiotype	Palladium

#### Table 1 | The Early Siderotype Processes

<sup>49</sup> Mike Ware, "The Technical History and Chemistry of Platinum and Palladium Printing" in Platinum and Palladium Photographs: Technical History, Connoisseurship, and Preservation, ed. Constance McCabe (Washington, D.C.: American Institute for Conservation of Historic and Artistic Works, 2017), 46–83.

The reader may be curious about kelainotype, which is unknown today. This process engaged much of Herschel's endeavor, because he found that it "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."<sup>11</sup> Given this eulogy, we might hasten to seek such specimens—but anyone who does so will discover that all known kelainotypes are now totally blank (see fig. 2d), yellowed rectangles of paper bearing no

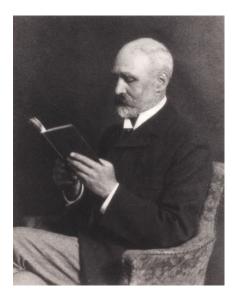


Figure 4. Photographer unknown, *Portrait of William Willis* (1841–1923), inventor of the Platinotype process, c. 1910. Platinum print,  $11 \times 8 \frac{3}{4}$  in. From Christie's, South Kensington, *19th and 20th Century Photographs*, sale cat., London, April 21, 1988, 38–39, lot 109.

discernible images! The reason for this sad loss is simple: elemental mercury is volatile, so the image just evaporates within a few days. Herschel's rueful comment was, "Most unfortunately, they cannot be preserved," and to this day the problem has not been overcome. The fading of kelainotypes—far from being an irrelevant digression—will prove important later when we consider the conservation problems of Sepia Platinotypes that use an additive of mercury.

## Researches of William Willis Jr.

Despite the best endeavors of the pioneers of photographic process, the goal of making prints in pure platinum did not show any promise of being achievable until 1872, when William Willis (Junior) of Bromley, Kent (fig. 4), took up the challenge in search of photographic image substances more enduring than silver. He was the elder son of William Willis (Senior), engraver and inventor of the "aniline" reprographic process (see technical highlight, Shannon Thomas Perich and Mike Ware, "William Willis's Transatlantic Connection: Alfred Clements"), and devoted himself to research in his private laboratory in Bromley in order to perfect his Platinotype process, which would absorb a further twenty years of his life. We shall see that, counting from the dawn of photography, more than fifty years were to elapse before a viable commercial platinum printing process became well established in 1892. But by 1917 the platinotype process had practically died out. Our first historical task therefore 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*?<sup>12</sup>

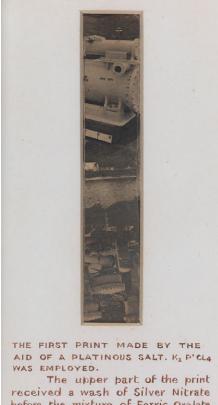
The first part of this twofold question can be answered in a single word: "chemistry," and the second part in another: "warfare." Willis's success depended upon his making three key chemical innovations in siderotype: discovering the correct choices of the platinum salt, the light-sensitive iron salt, and the developer. No one can expect to understand the historical development of the Platinotype process without some background in the chemistry of platinum; the essential relevant facts will now be exposed, step by step, in five chemical reactions.

Platinum occurs naturally as the elemental metal, which therefore 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* because it was also capable of dissolving the "royal metal," gold:

<sup>50</sup> Mike Ware, "The Technical History and Chemistry of Platinum and Palladium Printing" in Platinum and Palladium Photographs: Technical History, Connoisseurship, and Preservation, ed. Constance McCabe (Washington, D.C.: American Institute for Conservation of Historic and Artistic Works, 2017), 46–83.



Figure 5. William Willis, *The First Print in Pure Platinum*, 1872. National Media Museum, Bradford, UK, and Science & Society Picture Library, London.



before the mixture of Ferric Oxalate and Potassic Chloro Platinite was applied.

Figure 6. William Willis, *The First Print Made by the Aid of a Platinous Salt*. Patented 1873. National Media Museum, Bradford, UK, and Science & Society Picture Library, London.

platinum metal + *aqua regia*  $\rightarrow$  platinic chloride + nitric oxide 3Pt + 18HCl + 4HNO<sub>3</sub>  $\rightarrow$  3H<sub>2</sub>PtCl<sub>6</sub> + 8H<sub>2</sub>O + 4NO<sup>↑</sup>

The resulting salt of oxidized platinum(IV), previously called "platinic chloride" or "platinum perchloride," we now understand to be an acidic complex, dihydrogen hexachloroplatinate(IV) hexahydrate, H<sub>2</sub>PtCl<sub>6</sub>•6H<sub>2</sub>O. This was the only readily accessible compound of platinum known in the nineteenth century, and it therefore provided the starting material for all early experimentation in platinum chemistry. However, this substance is not readily reduced back to the metal; consequently it is not a satisfactory ingredient for a platinum printing process. Willis, in retrospect, described his first attempts of 1872 thus: "All my early experiments were naturally made with platinic chloride,"<sup>13</sup> and they resulted only in the lamentable object illustrated in figure 5. Then, in 1873, Willis had the idea of using the little-known platinous salts that are obtained by treating the usual platinic salts with a suitable chemical reducing agent:

platinic chloride + reducing agent  $\rightarrow$  platinous chloride Although platinous chloride had first been prepared by the German chemist Heinrich Gustav Magnus in 1828,14 his method was difficult and uncertain, so this salt remained a rare chemical until the 1870s. As Willis again recalled: "After a troublesome operation, I made some potassic chloroplatinite."<sup>15</sup> It is this compound, platinous chloride in its complex form as potassium chloroplatinite, K2PtCl4,16 that is essential to a successful platinum printing process because it is more easily reduced to the metal than platinic chloride, producing an image composed of "platinum black" (fig. 6). Willis's breakthrough was also important to the process of toning silver images with platinum: the photographic chemist Henry Chapman Jones later acknowledged that "it was not until potassium chloroplatinite was made available by Mr. Willis and the Platinotype Company that platinum toning was successful" 17 (see technical highlight, Ronel Namde and Joan M. Walker, "Platinum Toning of Silver Prints"). Indeed, Willis's finding a practical use for this expensive substance may account for the increased interest shown thereafter by chemists in devising easier syntheses of the little-known potassium chloroplatinite, using a variety of reducing agents, such as hydroxylamine:18

hexachloroplatinate + hydroxylamine  $\rightarrow$  tetrachloroplatinate + nitrogen PtCl<sub>6</sub><sup>2-</sup> + 2NH<sub>2</sub>OH  $\rightarrow$  PtCl<sub>4</sub><sup>2-</sup> + 2H<sub>3</sub>O<sup>+</sup> + 2Cl<sup>-</sup> + N<sub>2</sub>↑

Willis's second innovation was to employ the iron salt, ferric oxalate, which had shown a high sensitivity to light first discovered in 1831 by the German chemist Johann Wolfgang Döbereiner who, from that year, became Herschel's rival in photochemistry.<sup>19</sup> The exposure of ferric oxalate solution to light results in the precipitation of the insoluble yellow solid, ferrous oxalate, also known as the mineral Humboldtite:<sup>20</sup>

UV + ferric oxalate solution → ferrous oxalate solid + carbon dioxide gas hv + Fe<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> (aq) → 2FeC<sub>2</sub>O<sub>4</sub> (s)↓ + 2CO<sub>2</sub>↑

This uncommon salt did not feature in Herschel's siderotype experiments of 1842, which employed the more readily available ammonium ferric citrate,<sup>21</sup> although ferric oxalate was soon advocated by Robert Hunt

<sup>51</sup> Mike Ware, "The Technical History and Chemistry of Platinum and Palladium Printing" in *Platinum and Palladium Photographs: Technical History, Connoisseurship, and Preservation*, ed. Constance McCabe (Washington, D.C.: American Institute for Conservation of Historic and Artistic Works, 2017), 46–83.

in his famous treatise of 1844, *Researches on Light*.<sup>22</sup> As we have seen, the citrate suffices to produce images in gold, silver, and mercury, but does not provide a powerful enough reducing agent as photoproduct to enable a similar platinum printing process.

The third component essential for Willis's Platinotype process was a "developer" of hot, strong potassium oxalate solution, to dissolve the insoluble ferrous oxalate produced by light:

ferrous oxalate solid + oxalate  $\rightarrow$  soluble ferro-oxalate complex

$$\operatorname{FeC}_{2}O_{4}(s) + C_{2}O_{4}^{2-} \rightarrow \operatorname{Fe}(C_{2}O_{4})_{2}^{2-}(aq)_{2}^{2-}$$

which could then reduce the platinum salt to platinum metal. Willis 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 ferro-oxalate produces the platinum image by the following reduction:

ferro-oxalate + tetrachloroplatinate  $\rightarrow$  ferri-oxalate + platinum black  $2Fe(C_2O_4)_2^{2-} + PtCl_4^{2-} \rightarrow 2Fe(C_2O_4)_2^{-} + 4Cl^{-} + Pt\downarrow$ 

Thus, Willis's research overcame three chemical obstacles to the development of a viable Platinotype process: at the outset, he prepared the key platinum chemical, potassium chloroplatinite; secondly, he found the rare substance ferric oxalate to be an effective photosensitizer; and thirdly, a developer of hot potassium oxalate solution was necessary. But these only marked the beginning of the problems that Willis had to solve. The chemical reaction forming the platinum image is relatively slow; in consequence, some of the substances may be washed out of the paper during wet-processing before the reaction is complete, causing a loss in the quality of the image, which takes on a granular or fibrous appearance. Willis found it essential to use hot developer to accelerate the image-forming reaction. But, in order to achieve a fully developed picture, he was also obliged to compromise the elegant simplicity of his original idea by adding to his sensitizer formulation various salts of lead, silver, gold, or mercury, which, he found, assisted the image formation. A very early specimen of these experiments from 1873 is shown in figure 7. Analysis by Matthew L. Clarke in 2014 using x-ray fluorescence

spectrometry (XRF) has confirmed that the image contains platinum, silver, and gold.<sup>23</sup> Such uncertain mixtures-especially with silver contributing to the image-won very little public acceptance for Willis's new process, and the presence of these other metal salts left the Platinotype open to the criticism that it could be discolored by sulfides. Nonetheless, Willis took out a British patent on June 5, 1873, entitled Improvements in Photo-chemical Printing, which was greeted with editorial acclaim in the British *Journal of Photography (BJP)* of January 1874 as a "new printing process."24

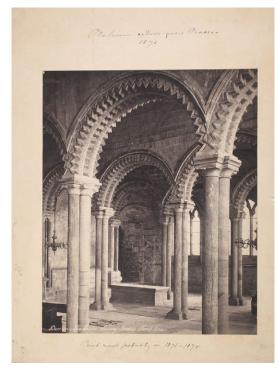


Figure 7. William Willis, Durham [cathedral], The Galilee [chapel], Showing Bede's Tomb. 501a, c. 1873– 74. Platinum-silver-gold print,  $21.2 \times 17.2$  cm. From a negative by an unknown photographer. National Gallery of Art, Photograph Conservation Department Study Collection, Gift of Hans P. Kraus, Jr.

Figure 8. William Willis Jr., Four Cadets in Front of Tent, 1877. Platinotype print,  $18.1 \times 23.7$  cm. From a negative by Pach Bros., c. 1865. This is the first Platinotype made in the United States. George Eastman Museum, Purchase, 1972.0199.0001.



Almost nothing was subsequently 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 precoated the paper with silver nitrate.<sup>25</sup> This was the year of Willis's first trip to the United States, and during his visit to New York, Willis himself made the first Platinotype in the United States (fig. 8). The original print, now in the collection of the George Eastman Museum (GEM), was examined by XRF in 2010 by Dusan Stulik and Tram Vo, who concluded that "Willis had made this particular photograph still using his original platinotype formula patented in 1873."<sup>26</sup> A reexamination of the print in 2015 by the photograph conservator Zachary Long at GEM has indeed proved that, to enhance the platinum image, not only did Willis's experimental prints, shown in figure 7. It appears that when making this historic "Platinotype" print in the United States, Willis was prudently "hedging his bets"!

Evidently, progress did not prove easy for Willis. His endeavors with Platinotype can be traced through six British patent specifications from 1873 to 1913,<sup>27</sup> which have been transcribed by Luis Nadeau in his valuable monograph on platinum printing.<sup>28</sup> In March 1878 Willis succeeded in eliminating the silver salt from his sensitized papers, but at the cost of adding some extra potassium chloroplatinite to the developer bath in order to sustain the image quality.<sup>29</sup> The first attested example of this advance is the remarkable double print shown in figure 1.<sup>30</sup> The verso of this print bears annotations in Willis's hand, first a penciled recipe, 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."<sup>31</sup>

Later in 1878, Willis patented, then publicized, this achievement of "altogether dispensing with the silver" in his process, although he did still find it necessary to continue adding the salt, lead(II) chloride. Apart from his two patents of 1873 and 1878, his first publication on the Platinotype process appears to be his August 1878 article in the *BJP*,

<sup>53</sup> Mike Ware, "The Technical History and Chemistry of Platinum and Palladium Printing" in *Platinum and Palladium Photographs: Technical History, Connoisseurship, and Preservation*, ed. Constance McCabe (Washington, D.C.: American Institute for Conservation of Historic and Artistic Works, 2017), 46–83.

in which he provided an explanation of its underlying chemistry.<sup>32</sup> Willis commended Platinotype for its permanence and the absence of any colloidal binder layer—qualities that, 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." 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! Four months later, Willis reinforced his first publication by performing a "practical demonstration of the working of his new Platinotype process" before a meeting of the Photographic Society of Great Britain on December 10, 1878,<sup>33</sup> and by publishing explicit formulas for his sensitizer and developer solutions.<sup>34</sup>

#### Willis's Platinotype Company of London

The technical advance of 1878 proved to be a turning point for Willis. Its only perceived weakness having been eliminated, the Platinotype process<sup>35</sup>—now silver-free—met with the approval of photographic chemists. So, in 1878 Willis was emboldened to found his Platinotype Company in order to market his sensitized papers commercially.<sup>36</sup> The company operated initially from Bromley in Kent,<sup>37</sup> but by 1883 it had established a sales office in central London,<sup>38</sup> and a factory at Penge in the suburbs.<sup>39</sup> The first commercial Platinotype papers became available in Britain in 1879,<sup>40</sup> with a choice of rough or smooth surface, on medium or thick paper at a price of one shilling for a demy sheet (17  $\frac{34}{22}$   $\frac{34}{4}$  inches).

Platinotypes were probably first seen publicly in London in 1879, at the 24th Annual Exhibition of the Photographic Society of Great Britain, where Willis—who was not an active camera user—exhibited twelve Platinotypes that he had personally printed from negatives by Frederick Hollyer, John Payne Jennings, Professor E. Stebbing, and Valen-tine Blanchard.<sup>41</sup> These prints were well thought of by the judges, receiving "honourable mention," and Platinotypes were also exhibited at the Royal Cornwall Polytechnic

Society, which awarded Willis its silver medal for his process in 1879.<sup>42</sup>

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.<sup>43</sup> He had been obliged to do this following the experiments conducted by John Spiller in February 1880 on the permanence of Platinotypes, in which the only reagent found to cause any damage at all was ammonium sulfide, reacting with the lead salt present to cause discoloration by lead sulfide.<sup>44</sup>

In his British Patent no. 1117 of 1880, Willis states that he used a single solution for coating, containing equal concentrations (60 gr/oz) of



Figure 9. Platinotype Company advertisement. From Capt. William de Wiveleslie Abney, *Photography with Emulsions*, 3rd ed. (London: Piper & Carter, 1885), n.p.

54 Mike Ware, "The Technical History and Chemistry of Platinum and Palladium Printing" in *Platinum and Palladium Photographs: Technical History, Connoisseurship, and Preservation*, ed. Constance McCabe (Washington, D.C.: American Institute for Conservation of Historic and Artistic Works, 2017), 46–83.

the two ingredients. This coating solution, containing 60 grains of potassium chloroplatinite ( $K_2PtCl_4FW=415.11$ ) per fluid ounce, has a concentration of 136.8 g/l of the substance and is 0.33 molar in platinum. The identical weight of ferric oxalate converts to a concentration of 0.57 molar in iron (assuming a formula of  $Fe_2(C_2O_4)_3$ •6H<sub>2</sub>O with FW=483.84). Willis also states that his paper contained "between 1.7 and 4 grains of  $K_2PtCl_4$  per square foot." This range of coating weight converts to 1.19 to 2.79 g/m<sup>2</sup> of  $K_2PtCl_4$  or a platinum metal coating weight of 0.557 to 1.311 g/m<sup>2</sup>. Quantitative elemental analyses for platinum and iron in specimens of unexposed papers from the Platinotype Company estimated the platinum metal coating weights of 0.518 and 0.611 g/m<sup>2</sup> for Willis's KK and AA papers, respectively.<sup>45</sup>

The photographic chemist George Dawson gave his technical appraisal of the newly improved process in 1880,<sup>46</sup> 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."<sup>47</sup> Earlier in 1880, James Young had demonstrated the Platinotype process to the Manchester Photographic Society and particularly commended it for the "engraving black" image color.<sup>48</sup>

By 1885, the Platinotype process had been awarded medals for excellence, including a Gold Medal at the International Inventions Exhibition (fig. 9).<sup>49</sup> Because the process was still protected by Willis's 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 license to practice platinum printing.<sup>50</sup> This tariff was suspended in 1888 after Willis launched his new "platinum-in-the-bath" method, protected by two more patents of 1887. 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 at room temperature, contained the usual potassium oxalate and all the potassium chloroplatinite.<sup>51</sup> Unfortunately, this was a recipe for chemical failure. This latest version of the process proved commercially 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."52 In response 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 mixed developer, which on storage quickly became black and unusable. Willis withdrew this "platinum-in-the-bath" method in 1892 when he launched his final and most successful version: "cold development" paper (table 2).53

#### Perfection of Platinotype by Cold Development

In 1892 Willis announced to the Camera Club of London that he had found a means to make Platinotype prints by development at room temperature rather than at the elevated temperatures that 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."<sup>54</sup> It is indeed regrettable 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 are known to have survived,<sup>55</sup> so that today the manufacture of his most successful commercial papers is a lost secret. We may infer

<sup>55</sup> Mike Ware, "The Technical History and Chemistry of Platinum and Palladium Printing" in *Platinum and Palladium Photographs: Technical History, Connoisseurship, and Preservation*, ed. Constance McCabe (Washington, D.C.: American Institute for Conservation of Historic and Artistic Works, 2017), 46–83.

Year and Reference	Code for Grade or Name	Paper Weight	Surface Texture	Color and Development
1879	None	Medium	Smooth	Black, hot bath
	None	Heavy	Rough	Black, hot bath
1883 <sup>a</sup>	None	Heavy	Smooth	Black, hot bath
1888 <sup>b</sup>		: all of the platinum nical; Willis suspends	,	n, which had very poor keeping qualities and was
1892 <sup>c</sup>	А	Medium	Smooth	Black, hot bath
	В	Heavy	Smooth	Black, hot bath
	С	Very heavy	Rough	Black, hot bath
	S	Medium	Smooth	Sepia, hot bath
1892 <sup>d</sup>		lopment: platinum s placed in 1893 by th	alt in sensitized paper e following system:	; no patent
1893 <sup>e</sup> 1896 <sup>f</sup>	AA	Medium	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 <sup>g</sup>	KK	Heavy	Smooth	Black, cold bath, higher contrast
1902 <sup>h</sup>	TT	Heavy	Rough	Black, cold bath, higher contrast
1906 <sup>i</sup>	Japine Sepia	Medium	Extra smooth, semi- glossy, and matt	Sepia, warm bath (100–120°F), parchmentized surface
1908 <sup>j</sup>	Japine Black	Medium	Extra smooth, semi- glossy, and matt	Black, cold bath, parchmentized surface
1908 <sup>k</sup>	and Sepia	The Platinotype Company's Revised List 1908 has only the following black papers for "cold development" and Sepia papers for "hot bath." NB: All black papers could also be "sepia developed" by the addition of the company's proprietary "Special Sepia Solution" to the developer.		
	AA	Medium	Smooth	Black, cold bath
	CC	Extra heavy	Rough	Black, cold bath
	КК	Heavy	Smooth	Black, cold bath, higher contrast
	TT	Heavy	Rough	Black, cold bath, higher contrast
	YY	Extra heavy	Smooth	Black, cold bath
	ZZ	Extra heavy	Slightly rough	Black, cold bath
	Japine KK	Heavy	Very smooth, semiglossy	Black, cold bath, parchmentized surface, higher contrast

# Table 2 | Dates and Descriptions of Platinotype Company Papers

#### Notes for Table 2

All are platinum papers, except where indicated in column 5. Years indicate earliest known reference, not timelines of use.

- a. Platinotype Company, *Instructions for Working the Platinotype Process*, 6th ed. (London: Platinotype Company, January 1883).
- b. Photographic News 32, no. 1557 (July 6, 1888): n.p.
- c. Platinotype Company advertisement for "Platinotype Papers," *British Journal Photographic Almanac, 1892*, 77.
- William Willis, "Recent Improvements in Platinotype," *Journal of the Camera Club* 6, no. 69 (1892): 53–55; no. 72 (1892): 19.
- e. Platinotype Company advertisement for "Platinotype," *Journal of the Camera Club* 7, no. 79 (August 1893): ix.
- f. "Platinotype Papers," *British Journal Photographic Almanac, 1896*, 106; Alfred Horsley Hinton, *Platinotype Printing* (London: Hazell, Watson & Viney, 1897), 7–8. *Op. cit.* 4th edn. 1904: 21–23; *idem*, "Platinotype Printing," in *The Barnet Book of Photography* (Barnet, Herts: Elliott & Son, 1898), 197–224.

#### (continued on following page)

- g. Willis & Clements, "The Platinotype," Photo-Miniature 4, no. 40 (1902): n.p.
- h. Willis & Clements, "TT Platinotype," Photo-Beacon 13 (January 1902): vi.
- Platinotype Company advertisement, Amateur Photographer 44 (August 21, 1906): xiv; Platinotype Company, "Sepia Japine Platinotype," British Journal Photographic Almanac, 1907, 23.
- j. "Black 'Japine' Platinotype Paper," *British Journal of Photography* 55, no. 2533 (November 20, 1908): 893–94.
- k. Platinotype Company, "Revised Price List of Platinotype Paper" (June 1, 1908), Harry Ransom Center, The University of Texas at Austin. See also Cassell's Cyclopaedia of Photography, ed. Bernard E. Jones (London: Cassell and Co., 1911), 418; Willis & Clements, The Platinotype: Simplest Photographic Process (Philadelphia: Willis & Clements, 1908), 14–15.
- 56 Mike Ware, "The Technical History and Chemistry of Platinum and Palladium Printing" in Platinum and Palladium Photographs: Technical History, Connoisseurship, and Preservation, ed. Constance McCabe (Washington, D.C.: American Institute for Conservation of Historic and Artistic Works, 2017), 46–83.

# Table 2 | Dates and Descriptions of Platinotype Company Papers

(continued from previous page)

Year and Reference	Code for Grade or Name	Paper Weight	Surface Texture	Color and Development
	Japine YY	Extra heavy	Very smooth, semiglossy	Black, cold bath, parchmentized surface
	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 <sup>l</sup>	Japine Sepia Buff stock		Very smooth	Buff paper, sepia, hot bath, parchmentized surface
	Sepia Buff stock		Matt	Buff paper, sepia, hot bath
	Buff stock		Matt	Buff paper, black, cold bath
1912 <sup>m</sup>	Ivory Black		Smooth and rough	Warm black, special hot (140°F) developer
1913 <sup>n</sup>	Satista		Smooth	Silver + platinum paper, black and sepia
1915°	Japine Silver		"Vellum"	Silver printing-out paper, brown to warm black, parchmentized surface
1916 <sup>p</sup>	Satistoid (later Satoid)	Medium heavy, extra heavy	Smooth and rough	Silver + platinum paper, brown; name changed to Satoid
1916 <sup>q</sup>	Sepia Japine K	Heavy	Very smooth	Sepia, hot bath, white stock, parchmentized surface
	Sepia Japine Y	Extra heavy	Very smooth	Sepia, hot bath, white and buff stock, parchmentized surface
1917 <sup>r</sup>	Sepia Japine Palladiotype		Very smooth	Palladium paper, brown, parchmentized surface
1918 <sup>s</sup>	Warm Black Palladiotype		Matt, smooth	Palladium paper, warm black color on white stock and on buff stock
1920 <sup>t</sup>	Satista Buff		Smooth	Silver + platinum paper, black and sepia on buff stock
1930 <sup>u</sup> 1936 <sup>v</sup>	· · ·	fore its closure the c 8, above. Additionall	, , , ,	the papers: AA, CC, KK, YY, KS, YS,
	KJ	Heavy	Very smooth	Black Japine, parchmentized surface
	KJS	Heavy	Very smooth	Sepia Japine, parchmentized surface
	CJB	Heavy	Very smooth	Black Japine on buff stock, parchmentized surface
	BJS	Heavy	Very smooth	Sepia Japine on buff stock, parchmentized surface
	BS	Heavy	Smooth	Sepia on buff stock
	CS	Heavy	Rough	Sepia, hot bath

#### Notes for Table 2

- Willis & Clements advertisement for "Platinum Papers—Buff Stock," *Photo-Miniature* 10, no. 115 (May 1911): n.p.
- m. Platinotype Company advertisement for "Ivory Black," British Journal Photographic Almanac, 1912, 19.
- n. William Willis, British patent no. 20022, September 4, 1913; "Satista Paper," British Journal of Photography 61, no. 2811 (March 20, 1914): 20; Willis & Clements advertisement for "Satista," Amateur Photographer Weekly 4, no. 90 (March 27, 1914): 315; Willis & Clements, Satista (Philadelphia: Willis & Clements, January 1914); Photo-Miniature 13, no. 154 (October 1916): 412; "Satista Matt Surface," Photo-Miniature 13, no. 155 (November 1916): n.p.
- o. "Japine Silver," Photographic Dealer 29, no. 234 (Nov. 1915): 381.
- p. Our Roving Commissioner, "A Sister to 'Satista'— 'Satistoid.' A Marvellous Production," *Photographic Dealer* 30, no. 238 (March 1916): 100–102; "Satista and Satoid," *Photo-Era* 10 (August 1916): 149.

- q. Platinotype Company, "Revised Price List of Platinotype Paper," 191; Willis & Clements, *The Platinotype: Simplest Photographic Process Producing Highest Quality Prints* (Philadelphia: Willis & Clements, 1916), 12–13.
- r. "Palladiotype," Amateur Photographer & Photographic News 65 (1917): 78.
- s. "Palladiotype (Matt Surface) Printing Paper," *British Journal of Photography* 65, no. 3019 (March 15, 1918): 128; "Matt Palladiotype," *British Journal of Photography* 65, no. 3024 (April 12, 1918): 169.
- t. Platinotype Company advertisement for "Satista," British Journal Photographic Almanac, 1920, 117.
- u. Owen Wheeler, *Photographic Printing Processes* (London: Chapman & Hall, 1930), 138–39.
- v. Transcript from label of a tin of Platinotype Company KK paper, dated 1936, Collection of the Museum of the History of Science, Oxford.
- 57 Mike Ware, "The Technical History and Chemistry of Platinum and Palladium Printing" in *Platinum and Palladium Photographs: Technical History, Connoisseurship, and Preservation*, ed. Constance McCabe (Washington, D.C.: American Institute for Conservation of Historic and Artistic Works, 2017), 46–83.

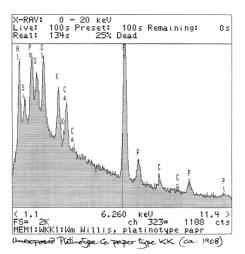


Figure 10. The first SEM-EDX spectrum, obtained in 1988, of unexposed KK paper from the Platinotype Company, dated 1906. Courtesy of Dr. Ashok Roy, Scientific Department, National Gallery, London.

ELECTRON HICROPROBE-EDX ANALYSIS: 1988-9. NATIONAL GALLERY, LONDON. COURTESY OF DUASHOK ROY.

from Willis's words that the key lay in the sizing or coating of the "ordinary platinotype paper" rather than any innovation in the chemistry of the sensitizer. High-quality papers made in Britain at the time were usually sized with a relatively impure grade of animal gelatin that inhibited the chemistry of Platinotype, as Willis had become aware from an early stage, c. 1880. He therefore avoided gelatin as a sizing agent for his papers and looked abroad to papers made in Germany and France: the "*papier de Saxe*" from Steinbach's mill in Malmedy and later the papers of Blanchet Frères et Kléber (BFK) in Rives, which were all sized with alum-rosin and starch, as described in the essays by Cyntia Karnes and Sarah S. Wagner. However, Willis's patents, being typically "economical with the truth," say nothing of this important choice.

The success of 1892 must have entailed some additional feature, possibly the use of a retentive, acidic alum-rosin sizing for the paper and possibly the inclusion of a clay filler that slowed up the rate of dissolution of the exposed sensitizer during wet processing and allowed a full development of the image. The use of these additives in papermaking is fully discussed in Karnes's essay. In 1989 a specimen of the Platinotype Company's KK paper (see table 2), from a previously unopened tin dating from 1906 acquired by the author, 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, with the results shown in figure 10. Later analysis of the KK paper by x-ray fluorescence spectrometry (XRF) by Jacqueline Rees at the Victoria & Albert Museum, London, in 1993,<sup>56</sup> additionally showed the presence of zinc and lead at low levels. In 2011 the same paper was again examined by XRF by Clarke at the National Gallery of Art (NGA), Washington D.C., and traces of the additional elements chromium and barium were detected.<sup>57</sup> All the elements detected and their suggested origins are summarized in table 3. Preliminary spot tests on the KK paper in 1989 had suggested the presence of an alum-rosin sizing agent.<sup>58</sup> This inference was recently confirmed as part of the modern investigation at the NGA by Christopher Maines using GC-MS instrumental analysis: "Using pyrolysis and gas chromatography with mass spectrometry, and in situ methylation by tetramethylammonium hydroxide, 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 a diterpenoid, abietic acid, i.e. rosin."59 Maines further notes that there were no aminoacids (i.e., no proteins: gelatin or albumen) and no gums. The only carbohydrate was glucose (the

<sup>58</sup> Mike Ware, "The Technical History and Chemistry of Platinum and Palladium Printing" in *Platinum and Palladium Photographs: Technical History, Connoisseurship, and Preservation*, ed. Constance McCabe (Washington, D.C.: American Institute for Conservation of Historic and Artistic Works, 2017), 46–83.

monomer from cellulose and starch). GC-MS analysis could not confirm the presence of starch as the iron and platinum salts in the paper interfered with the analysis.<sup>60</sup> However, an iodine spot test using 5% w/v iodine and 10% w/v potassium iodide in water (Lugol's Solution) performed by Sarah S. Wagner at the NGA showed the presence of starch in KK, AA, and Japine papers, indicating that these Platinotype Company papers were sized with alum-rosin-starch and did not contain a coating of protein as had been previously hypothesized.<sup>61</sup>

Historically, alum-rosin internal sizing, also called "engine sizing," is carried out during the beating of the paper pulp,<sup>62</sup> before formation of the sheet, by addition of an alkaline solution of rosin, called rosin soap, containing the sodium salt of abietic acid, which is water soluble and was frequently used with starch.<sup>63</sup> The pulp is then acidified by treatment with alum (potassium aluminum sulfate), which forms hydrogen ions by hydrolysis of the hydrated aluminum(III) cation:

 $Al(H_2O)_6^{3+} \Rightarrow Al(H_2O)_5(OH)^{2+} + H^+ \Rightarrow Al(H_2O)_4(OH)_2^+ + 2H^+ \Rightarrow etc.$ causing the precipitation within the fibers of the insoluble, hydrophobic abietic acid, for which the aluminum ions also act as a mordant to the cellulose, probably binding to the hydroxylic functions. The presence of aluminum and silicon in the SEM-EDX spectrum of Willis's KK paper (see fig. 10) is consistent with an aluminosilicate clay such as kaolinite, although the aluminum will come in part from the alum-rosin size.

To return to our narrative in 1892: 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 that his process was "permanent," "artistic," and "the simplest" (fig. 11). Let us make a preliminary assessment of his threefold claim.

Photographic impermanence had been a long-standing issue even before an 1855 committee of the Photographic Society recommended<sup>64</sup>—but not unanimously—that silver prints should be gold-toned for permanence.<sup>65</sup> Willis's research had been stimulated in the first place by his quest for an image substance more permanent than silver. Although the metal constituting a Platinotype image is indeed quite invulnerable, its

Element	Symbol	Possible Origin
		Major Constituents
Aluminum	Al	Alum (potassium aluminum sulfate) sizing hardener; aluminosilicate (clay paper filler)
Silicon	Si	Aluminosilicate (clay paper filler), e.g. kaolinite
Platinum	Pt	Potassium tetrachloroplatinate(II) sensitizer
Chlorine	Cl	Potassium tetrachloroplatinate(II) sensitizer
Potassium	К	Potassium tetrachloroplatinate(II) sensitizer; alum
Iron	Fe	Ferric oxalate sensitizer
Calcium	Ca	Paper additives: chalk (calcium carbonate); gypsum
Sulfur	S	Sulfate in alum or gypsum (calcium sulfate)
		Minor Constituents
Lead	Pb	Willis's additive of lead(II) chloride
Copper	Cu	Paper impurity? brass from blades of Hollander beater?
Zinc	Zn	White pigment?
Chromium	Cr	Dichromate contrast enhancement additive?
Barium	Ва	Baryta white pigment (barium sulfate)

Table 3 | Elements Detected in Platinotype Company KK Paper of 1906

59 Mike Ware, "The Technical History and Chemistry of Platinum and Palladium Printing" in Platinum and Palladium Photographs: Technical History, Connoisseurship, and Preservation, ed. Constance McCabe (Washington, D.C.: American Institute for Conservation of Historic and Artistic Works, 2017), 46–83. paper substrate, unfortunately, is not: the besetting problem that Platinotypes present to the conservator is acidic embrittlement of the cellulose paper sheet. The buildup of acid was exacerbated by the catalytic action of the platinum black itself on sulfurous gases, which were commonly present in polluted Victorian atmospheres. The other characteristic feature of deterioration in platinum prints is a slow appearance of yellow discoloration in the highlights. There are many articles in the photographic literature complaining of yellow stains, presumed to be due to incomplete removal of the iron(III) salts, and offering suggestions for curing this, usually by rather aggressive bleaching agents,<sup>66</sup> as related

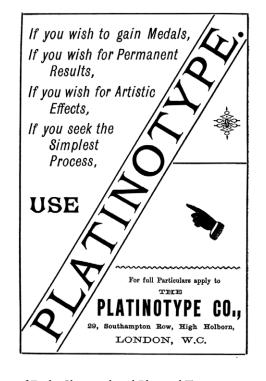


Figure 11. Platinotype Company advertisement. From *The Year-Book of Photography and Photographic News Almanac,* 1898, vi.

in the essay by Erin L. Murphy, "A Summary of Early Chemical and Physical Treatments of Platinum Prints." The occurrence of stain has been simulated experimentally by accelerated aging, as described in the essay by Matthew L. Clarke, "Characterization, Degradation, and Analysis of Platinum and Palladium Prints," and an hypothesis for the mechanism of its slow formation is put forward in the essay by Constance McCabe et al., "Alfred Stieglitz's Palladium Prints: Treated by Steichen"; modern conservation treatments for this problem are considered in the essay by Matthew L. Clarke and Dana Hemmenway.

Willis's "artistic" claim was also debatable: the Platinotype, with its neutral gray-black tones and totally matte surface, arrived at a time when the public taste in photographs had already been conditioned by an aesthetic of the highly glossy, purplish-brown, goldtoned albumen print-the dominant photographic print medium of the previous four decades. The neutral tones of Platinotype were often viewed with distaste.<sup>67</sup> Although the general public tended at first to shun the Platinotype for its "unphotographic" appearance, there were connoisseurs such as William Kinninmond Burton who appreciated its fine engraving black without "meretricious gloss."68 John Nicol also favored the neutral colour of Platinotype and commended its permanence.<sup>69</sup> Herbert Bowyer Berkeley, a partner with Willis in the Platinotype Company until 1889,<sup>70</sup> expressed his views quite vigorously: "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."71 Alfred Horsley Hinton also referred disparagingly to the glossy surface of albumen papers.<sup>72</sup> Nevertheless, the loss of brilliance and shadow depth on drying a plain paper Platinotype induced some practitioners to resort to waxing or varnishing their prints after processing. The conservator Clara von Waldthausen has described the various materials recommended in this practice,<sup>73</sup> which could include jelly size, varnish, beeswax, or water megilp.<sup>74</sup> Willis's commercial awareness of popular public taste induced him to devise and market new varieties of Platinotype paper furnishing prints with brown images-"Sepia Platinotype," or semiglossy surfaces and "Japine papers," or even both features, "Japine Platinotype for Sepia Tones," all of which are described below (see table 2).

<sup>60</sup> Mike Ware, "The Technical History and Chemistry of Platinum and Palladium Printing" in *Platinum and Palladium Photographs: Technical History, Connoisseurship, and Preservation*, ed. Constance McCabe (Washington, D.C.: American Institute for Conservation of Historic and Artistic Works, 2017), 46–83.

Regarding the claim of simplicity for Platinotype, there can be no doubt that the *modus operandi* was certainly much easier than silver printing-out papers, which required three times the exposure, very careful wet processing and fixing, gold toning, and washing for permanence. By contrast, a finished platinum print could easily be obtained in half an hour or less. Photographic manuals of the day show how popular the process had become and strongly recommended it for beginners: "Platinotype is the simplest and quickest process of printing."<sup>75</sup>

#### Willis & Clements Company of Philadelphia

On his first visit to the United States in 1877, mentioned above, William Willis (Junior) formed a partnership with an expatriate Briton, Alfred Clements,76 who ten years previously had been employed by William Willis (Senior) in England, as described in the highlight by Perich and Ware. Clements undertook to introduce the Platinotype process to photographers in the United States.<sup>77</sup> Setting up business in New York, he sought commissions to print Platinotypes by enlargement, which was a technically demanding use of the medium, as is described in Greta Glaser's essay. Clements encountered many difficulties, not least the explosion of a boiler on December 17, 1880, which destroyed all of the equipment in the New York office.<sup>78</sup> In 1881 Clements gave up his enterprise in New York, sold off the whole Platinotype enlarging business, and relocated to Philadelphia.<sup>79</sup> There he devoted his side of the business to retailing the chemicals for the Platinotype process and, since it was by then protected by U.S. patents, to the licensing of photographers in the United States to hand-sensitize paper for their own use. An 1881 advertisement for the new business records that Thomas H. McCollin was appointed sole trade agent,<sup>80</sup> which was probably a shrewd choice, in view of his established reputation as a Philadelphia dealer in photographic materials, with a well-known catalog, and by 1890 McCollin was also the managing editor of the American Journal of Photography.

William Willis then made a second transatlantic trip in order to supervise personally the establishment of Willis & Clements in Philadelphia. He addressed the Photographic Society of Philadelphia on February 3, 1881, and conducted a public demonstration of the chemistry underlying his Platinotype process.<sup>81</sup> However, some years elapsed before the Philadelphia company began to import Willis's presensitized papers from Britain. An early instruction booklet of 1885 shows that Willis & Clements Company was still confining itself to retailing the sensitizer chemicals and paper needed to selfcoat platinum paper, together with other minor items of equipment.<sup>82</sup> The company prescribed different formulations for contact printing as opposed to projection printing using a solar enlarger (see the essays by Glaser and Lee Ann Daffner). 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 expensive absorbers of the sensitizer solution), with the intention of photographically decorating "d'oyleys, mats, banner-screens, antimacasssars, cosies, mantel-cloths, &c."83 (see technical highlight, Ronel Namde, "Platinum Printing on Textiles"). Silks and satins were not recommended unless they contained very little fabric dressing; evidently silk proved a more difficult substrate for Platinotype. Alfred Clements made a visit to Europe in 1886,84 following which the Willis & Clements Company finally began to import some of the sensitized papers of the Platinotype Company of London<sup>85</sup> and to market them in the United States in 1888.<sup>86</sup>

61 Mike Ware, "The Technical History and Chemistry of Platinum and Palladium Printing" in *Platinum and Palladium Photographs: Technical History, Connoisseurship, and Preservation*, ed. Constance McCabe (Washington, D.C.: American Institute for Conservation of Historic and Artistic Works, 2017), 46–83.

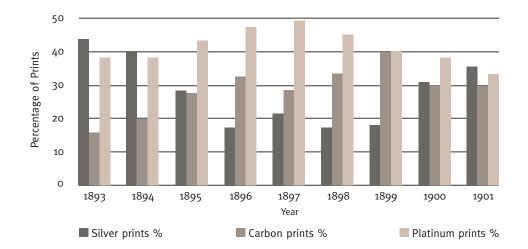


Figure 12. Relative numbers of prints in silver, carbon, and platinum, at Royal Photographic Society Exhibitions, 1893–1901. Data from H. V. Hyde, "Some Exhibition Statistics," *Photographic News* 45 (1901): 680.

# Notable Early Users of Platinotype

It was not until the innovation of the "cold development" process of 1892 that Platinotype became generally acclaimed by the British photographic press, thus ensuring that Willis's product enjoyed a much wider use. By 1895, the salon walls in Britain were exhibiting more Platinotypes than any other photographic process; the medium rapidly achieved preeminence for art photography. As quantitative evidence for this claim, there are some exhibition statistics in figure 12, which displays the relative numbers of prints in three media—silver, carbon, and platinum—shown at the prestigious Annual Exhibitions of the Royal Photographic Society between 1893 and 1901.<sup>87</sup> The bar chart shows that between a half and a third of the work displayed during those years was in platinum, the nearest competitor being carbon, with a quarter to a third of the total.

The excellence of a process is reflected in the good opinions of its most accomplished users, so any list of the distinguished practitioners of Platinotype must read like a "Who's Who" of Pictorialism. In particular, Platinotype became the favored medium of the Brotherhood of the Linked Ring.<sup>88</sup> Notable users included Frederick Henry Evans (1853–1943), whose great series of cathedral interiors was begun in 1890, printed only in Platinotype.<sup>89</sup> The leading Pictorialist, Henry Peach Robinson (1830–1901), had his most important exhibition work rendered in Platinotype.<sup>90</sup> Other notable British photographs in Platinotype were the portraits by Frederick Hollyer (1838-1933), 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 critical doyen of art photography, showed an early enthusiasm for Platinotype,<sup>91</sup> declaring: "we emphatically assert that the platinotype process is *facile princeps*." <sup>92</sup> His most outstanding contribution to the canon was his album of forty Platinotypes coauthored in 1886 with artist Thomas Goodall (1857-1944), entitled Life and Landscape on the Norfolk Broads, which is the subject of the essay by Philippa Wright and John Taylor.

A few high-quality books soon employed Platinotype for their illustrations.<sup>93</sup> In 1881 William Willis self-published an album of Platinotypes of personal travel sketches from 1877–78 called *Willis's Pencillings in Wales*, which bore an explanatory preface, inscribed and signed in his own hand.<sup>94</sup> In 1884 Edward Bradbury's popular tourist guidebook, *All about Derbyshire*,<sup>95</sup> 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 (see fig. 17).<sup>96</sup>

<sup>62</sup> Mike Ware, "The Technical History and Chemistry of Platinum and Palladium Printing" in *Platinum and Palladium Photographs: Technical History, Connoisseurship, and Preservation*, ed. Constance McCabe (Washington, D.C.: American Institute for Conservation of Historic and Artistic Works, 2017), 46–83.

By the close of the century, the Platinotype process had reached the zenith of its popularity, being widely acknowledged as the finest printing medium in the entire photographic repertoire. Platinotype Company papers were used in the United States during the 1890s by their chief advocate, Alfred Stieglitz,<sup>97</sup> the most notable American photographic artist and leading light of the Photo-Secession movement, which he founded in 1902. More about the practices and achievements of Stieglitz can be found in the essays by Sarah Greenough and McCabe et al.

Platinum was also esteemed as an appropriate medium for copying famous works of art; Frederick Hollyer, especially, published many reproductions in Platinotype, both of old masters and of the work of his contemporaries in the Pre-Raphaelite Brother-hood.<sup>98</sup> By 1897, Hollyer's American agent was none other than Alfred Clements, who had assumed the business title of "The London Art Publishers,"<sup>99</sup> and in this guise offered prints made on "Willis & Clements Platinotype paper" (fig. 13).<sup>100</sup> A further tribute to the prestige enjoyed by the platinum print for reproduction purposes is represented by the publication around 1910 by Eyre & Spottiswoode of a *Catalogue of Sepia Platinotype Reproductions of Famous Pictures*, which offered a choice of some five hundred celebrated titles.

## Sepia Platinotype and the Effect of Mercuric Salts

It is sometimes mistakenly stated that sepia Platinotypes were simply made historically by employing a hot developer bath, at c. 160°F (71°C).<sup>101</sup> However the degree of "warming" of the neutral gray-black color 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 to the black variety. His patent descrip-

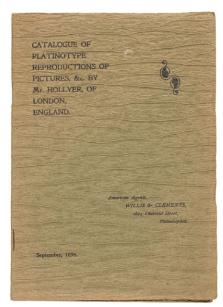


Figure 13. Cover of Willis & Clements, American Agents, *Catalogue of Platinotype Reproductions of Pictures, &c. by Mr. Hollyer, of London, England*, featuring Willis & Clements Platinotype paper, 18 × 13 cm. (Philadelphia: Willis & Clements, September 1896). National Gallery of Art Library, Department of Image Collections, Album P167.

tion of 1878 states 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 procedure was the occurrence of a change in color between the neutral black shadows and the yellowed highlights, which Willis called "double tones" and deemed aesthetically unacceptable. (The phenomenon of dichroism should not be confused with tonal reversal or "solarization" due to heavy exposure, and possibly the presence of palladium, in which the darkest shadow tones reverse to brown and the light tones are more neutral.) This may explain why Sepia Platinotype is not mentioned in the earliest advertisements and instructions from the Platinotype Company; it was probably first marketed c. 1885, to judge by company literature. Willis overcame the problem of "double tones" by incorporating the mercuric chloride in the sensitized coating of the paper. 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 but presumably containing a mercury(II) salt) 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" — also presumably mercury(II)containing. However, in 1892 it transpired that Willis's new "cold development" process for black paper was not applicable to his sepia papers, despite his best endeavors in that direction; his publication admits that "he was, however, doubtful whether sepia would ever be obtained under a temperature of 150°F."<sup>102</sup> 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."<sup>103</sup> The Platinotype Company product lists of 1894 and 1906 continued to designate it as "sepia hot bath paper," which still had to be developed at 160–170°F (71–77°C).

In his important review of 1911,<sup>104</sup> the Platinotype Company manager William 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 paper, the color 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."<sup>105</sup> At a later meeting in 1915, Smith showed severely faded specimens of mercury-developed Platinotypes to demonstrate his point.<sup>106</sup> In spite of this warning, he still described the addition of modest amounts of mercuric chloride to the developer in order to warm the otherwise neutral image color of black platinotype, and many practitioners of the day did indeed resort to this practice, as it was also recommended by Paul Anderson in 1917 (see below, and the additives tables by Alice Carver-Kubik et al.).<sup>107</sup> Meanwhile, Baron Arthur von Hübl in the second edition (1902) of his work, Der Platindruck, <sup>108</sup> had described a novel formulation that finally enabled the cold development of sepia papers by using mercuric citrate rather than mercuric chloride in the sensitizer. This was taken up by Heinrich Kühn in 1910, as described in Andreas Gruber's essay, and the recommendation eventually reached the popular handbooks.<sup>109</sup>

In 1986 the first scientific study of platinum printing in modern times tested the consequences of using mercury(II) salts by preparing a platinum sensitizer containing mercury(II) nitrate at an equimolar concentration to the platinum(II) and exposing it for a range of times in the usual way.<sup>110</sup> The amounts of mercury and platinum in the fully processed prints were measured by quantitative x-ray fluorescence spectrometry (XRF) and compared with the equal amounts measured in the unexposed sensitized paper. It was found that mercury(II) is reduced much more readily than platinum(II), so the proportion of mercury in the final image is always higher than in the sensitizing solution (1:1), the ratio Pt:Hg being 1:4 at low exposures (high tonal values) and 1:2 at high exposures (shadow tones). In recent research, Saori Kawasumi Lewis has prepared platinum papers by the traditional recipe, including mercuric chloride in the sensitizer, in the developer, and in both.<sup>111</sup> Comparison of step-tablet exposures shows clearly how the presence of mercury-in all cases-imparts a warmer tone and a longer exposure scale than platinum alone displays, but the use of mercury salt in the developer leaves a much higher proportion of mercury in the image than incorporating the mercury salt in the sensitizer, with corresponding implications for the failure of its longevity (see Clarke, "Characterization, Degradation, and Analysis of Platinum and Palladium Prints").

The precise mechanism by which mercury imparts a sepia tone to platinum prints has yet to be established. Warmer image color can result from smaller particle size, according to Gustav Mie's theory of light-scattering by metal nanoparticles,<sup>112</sup> but it is not clear why mercury should diminish the platinum particle size since it does not form an amalgam with platinum. All historic sepia platinotypes so far examined by XRF appear to contain mercury, at a concentration that correlates with image optical density, so it seems that mercury is *necessary* for the color, but it is evidently not *sufficient* because many black platinotypes have also been found by XRF analysis to contain mercury. However, XRF provides no information on the chemical state of the element detected. Mercury may be present as the elemental metal, or it may be present as a compound such as the insoluble colorless salt mercury(I) chloride, Hg<sub>2</sub>Cl<sub>2</sub>, which might account for these disparate observations.

<sup>64</sup> Mike Ware, "The Technical History and Chemistry of Platinum and Palladium Printing" in *Platinum and Palladium Photographs: Technical History, Connoisseurship, and Preservation*, ed. Constance McCabe (Washington, D.C.: American Institute for Conservation of Historic and Artistic Works, 2017), 46–83.

# The Platinotype Company's Range of Papers

A description of the operations of the newly formed Platinotype Company was published in Henry Baden Pritchard's 1882 volume The Photographic Studios of Europe.<sup>113</sup> Some idea of the professionalism of Willis's production methods also comes from reports in the photographic press of open days at his Penge works.<sup>114</sup> By 1892, the company was selling Platinotype papers in nine sizes, precut to match the negative formats then current, at a unit cost of c. 8 d/ft<sup>2</sup>—a price that remained constant over the next fifteen years<sup>115</sup> and may be compared with the cost of c. 3 d/ft<sup>2</sup> for silver printingout papers and 6 d/ft<sup>2</sup> for the new bromide enlarging papers.<sup>116</sup> 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, 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 sulfite, which enabled the development of camera negatives to greater density ranges without fogging, so providing a better match to the long exposure scale (c. 2) of the platinotype process. The company marketed this important innovation in 1882 as the very first proprietary developer, "Sulpho-pyrogallol."<sup>117</sup>

The weights, surfaces, and image colors of papers available at various stages in the Platinotype Company's history are summarized in table 2. These were alphabetically coded to indicate their "grade": by a single letter to designate hot-bath papers, a doubled letter for cold-development papers, and including "S" in the code to indicate the sepia papers that incorporated a mercury(II) salt in the sensitizer and required a hot-bath oxalate developer. Later, code letter "J" designated Japine papers (see below) and "B" was used to indicate papers of buff stock.

Around 1900, the pure chemical potassium chloroplatinite was manufactured chiefly by the leading British precious-metal refiner, the Johnson Matthey Company, which supplied it to Willis for the manufacture of Platinotype paper. The sales figures for this product were discovered in the Johnson Matthey Company records by Ian Cottington, and they show that the sales reached a peak in 1905 (fig. 14).<sup>118</sup> 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

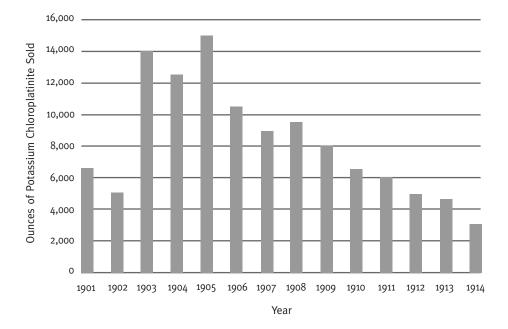


Figure 14. Sales of potassium chloroplatinite by Johnson Matthey, 1901–1914 (in ounces). Data from Ian Cottington, "Platinum and Early Photography," *Platinum Metals Review* 28, no. 4 (1984): 178–88, reprinted in *History of Photography* 10, no. 2 (1986): 131–39.

<sup>65</sup> Mike Ware, "The Technical History and Chemistry of Platinum and Palladium Printing" in *Platinum and Palladium Photographs: Technical History, Connoisseurship, and Preservation*, ed. Constance McCabe (Washington, D.C.: American Institute for Conservation of Historic and Artistic Works, 2017), 46–83.

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:<sup>119</sup> 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. There are 480 grains in a Troy ounce. The total area of Platinotype paper manufactured during these fourteen years is hence easily calculated and would have sufficed to produce about 35 million whole-plate prints during Platinotype's heyday. The absence today of a substantial proportion of these suggests two possibilities: either that the process was more fal-



Figure 15. Dr. E. Hornig, [*untitled portrait*], c. 1882. Platinum print made by the process of Giuseppe Pizzighelli and Arthur von Hübl, 13.8 × 10.3 cm. From a negative by V. Angerer. From E. Hornig, *Photographica: Blätter zur Illustrirung photographischer Verfahren*, vol. 4, *Platinotypie* (Vienna and Leipzig: Verlag der Photographischen Correspondenz, 1882), n.p. Courtesy of George Eastman Museum collection.

lible than usually represented and much spoiled paper ended up in the wastebin, or that there are many historic Platinotypes in collections still lying unrecognized as such.

**Giuseppe Pizzighelli and Arthur von Hübl: The "Printout" Platinum Process** In 1882 two Austrian army captains in the photographic department of the military technical administration, Giuseppe Pizzighelli and Baron Arthur von Hübl, published detailed recipes and instructions, in German, for their version of platinum printing.<sup>120</sup> The Vienna Photographic Society awarded its Voigtländer Prize to the authors for this publication, which was soon translated from German into both French<sup>121</sup> and English.<sup>122</sup> It opened up the technique by making practical details and formulas more accessible to all (fig. 15) and may well have been responsible for the emergence of some commercial competition to Willis's erstwhile monopoly, as described in the essay by Wagner on the history of commercial platinum papers.

In 1887, Pizzighelli, by then working alone in Benjaluka, Bosnia, made a significant addition to the canon: he devised an alternative iron sensitizer formulation that yielded a printed-out platinum image directly on exposure, needing no developer, only bathing the print in dilute hydrochloric acid to clear the unexposed sensitizer, followed by washing in water.<sup>123</sup> The key to this "direct printing platinotype" process, as it was then called,<sup>124</sup> was the use of the "double salt" sodium ferric oxalate for the sensitizer, rather than ferric oxalate. Pizzighelli also described the similar results of testing ammonium ferric oxalate.<sup>125</sup> The substance of this Austrian discovery was quickly translated and relayed to the English-speaking readership of the Amateur Photographer by Alfred Stieglitz, then resident in Germany.<sup>126</sup> These "double salts" were not new: they had been used in siderotype photography for many years as alternatives to ferric oxalate.<sup>127</sup> Hermann Halleur had described the use of ammonium ferric oxalate to make silver prints as early as 1853,<sup>128</sup> and Charles Burnett and John Mercer were separately using it by 1858; it was advocated for the cyanotype process by Carey Lea in 1863,<sup>129</sup> and later by J. Traill-Taylor in 1889.130 Pizzighelli's "direct printing" or "water developed" platinotype was taken up by a number of Continental manufacturers, such as Adolf Hesekiel & Company, in Berlin, with its "Dr. Hesekiel's Platina Direct Printing Paper." However, after an initial flush of commercial enthusiasm, these papers did not remain on the market for very long, possibly for reasons of limited storage life and, unlike Willis's products, the need to control their humidity during exposure for consistent results.

<sup>66</sup> Mike Ware, "The Technical History and Chemistry of Platinum and Palladium Printing" in *Platinum and Palladium Photographs: Technical History, Connoisseurship, and Preservation*, ed. Constance McCabe (Washington, D.C.: American Institute for Conservation of Historic and Artistic Works, 2017), 46–83.

We can understand the photochemistry of printout platinotype once armed with the present-day chemical knowledge that these so-called "double salts" are, in fact, complexes of iron(III) coordinated by three oxalate ligands in the anion:  $Fe(C_2O_4)_3^{3-}$ . This anion undergoes a photochemically induced redox reaction similar to ferric oxalate (see above), but immediately yields the soluble oxalato-complex of iron(II):

UV + ferri-oxalate → ferro-oxalate + carbon dioxide gas  

$$h\nu + 2Fe(C_2O_4)_3^{3-} \rightarrow 2Fe(C_2O_4)_2^{2-} + C_2O_4^{2-} + 2CO_2$$

Provided that the paper is sufficiently humid (in equilibrium with an atmosphere of 70–80% RH), local migration of the ions is sufficient to form the platinum image immediately, without additional oxalate "developer":

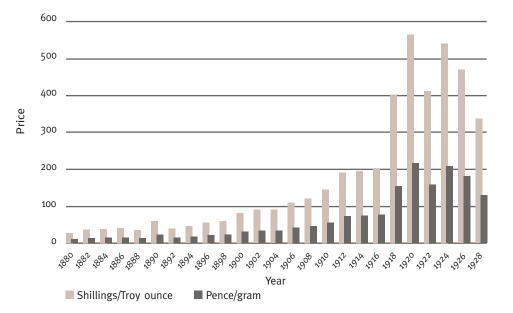
ferro-oxalate + tetrachloroplatinate  $\rightarrow$  ferri-oxalate + platinum black

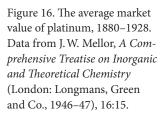
 $2\operatorname{Fe}(\operatorname{C_2O_4)_2^{2-}} + \operatorname{Pt}\operatorname{Cl_4^{2-}} \rightarrow 2\operatorname{Fe}(\operatorname{C_2O_4)_2^{-}} + 4\operatorname{Cl^-} + \operatorname{Pt} \downarrow$ 

Practical details of formulas for hand-coating papers were later also published by the leading British photographic scientists, William de Wiveleslie Abney and Lyonel Clark in their 1895 treatise *Platinotype: Its Preparation and Manipulation*.<sup>131</sup> In the same year, Baron Arthur von Hübl published his comprehensive practical handbook, *Der Platindruck*, in German, followed by a second edition in 1902.<sup>132</sup> This notable treatise has, regrettably, remained untranslated into English, other than a selective four-part "digest" by E. J. Wall.<sup>133</sup>

#### Platinum Catalysis: Friedrich Wilhelm Ostwald's "Catatype"

It had been known since the 1820s that platinum metal—especially when finely divided as sponge or powdered platinum black—was a prime exhibitor of the important chemical phenomenon of catalysis. Döbereiner employed it in 1823 to ignite a flame of hydrogen gas in a formidable table lighter of his own devising, called his *Platinfeuerzeug*. More significantly, in 1902, the foremost German physical chemist, Friedrich Wilhelm Ostwald, discovered the ability of platinum to catalyze the oxidation of ammonia to nitric acid.<sup>134</sup> Previously produced from imported saltpeter (potassium nitrate) or Chile saltpeter (sodium nitrate), nitric acid is essential to the manufacture of explosives such as picric acid (trinitrophenol), TNT (trinitrotoluene), nitroglycerine, and the fertilizer, or explosive, ammonium nitrate. The future strategic importance of a supply of nitric acid placed a premium on the precious metal itself. The discovery of catalysis by platinum had huge commercial consequences and led to an exponential rise in the metal's price, as may be seen in figure 16.





<sup>67</sup> Mike Ware, "The Technical History and Chemistry of Platinum and Palladium Printing" in *Platinum and Palladium Photographs: Technical History, Connoisseurship, and Preservation*, ed. Constance McCabe (Washington, D.C.: American Institute for Conservation of Historic and Artistic Works, 2017), 46–83.

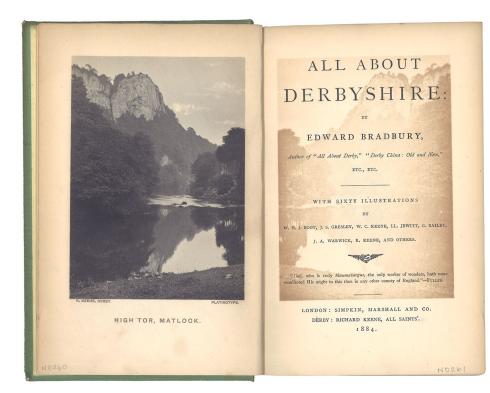


Figure 17. Richard Keene, *High Tor, Matlock*, 1884. Platinotype, 12.5 × 9 cm. From Edward Bradbury, *All about Derbyshire* (London: Simpkin, Marshall and Co., 1884), frontispiece.

Ostwald's discovery would eventually undermine the commercial viability of the Platinotype medium; catalysis was highly beneficial for the chemical industry, but it spelled the beginning of the end for the first phase of platinum photography. Willis was obliged to seek ways of countering the rising cost of his raw materials while maintaining the appeal of his products, and so the rest of this history will be chiefly concerned with the various types of photographic paper that Willis evolved in that endeavor, as summarized chronologically in table 4.

Ironically, it was Ostwald who also devised in 1903 a reprographic process called "catatype" that employed a platinum print as a template to catalyze a colorizing reaction. A fully processed platinum print was closely contacted with a paper surface impregnated with an unstable chemical combination of oxidant and reductant,<sup>135</sup> so the platinum black catalyzed their chemical reaction to produce a red coloration; such an image could be offset repeatedly to make multiple prints from the platinum print.<sup>136</sup> A related manifestation of the catalytic power of platinum black is seen in the phenomenon of the slow offsetting of a brownish-yellow positive image in a sheet of paper that has prolonged contact with a facing platinum print. This is a phenomenon without a name, for which the author suggests the term "autoplatinography." It is often seen opposite Platinotypes bound into albums or books (fig. 17).<sup>137</sup> The degradation of the facing paper is believed to be catalyzed by the platinum image; evidence from recent experiments to simulate this effect is presented in the essay by Jennifer K. Herrmann et al.

## Willis's Japine Papers and Their Analysis

In 1906 Willis launched one of his most successful commercial variants on Platinotype, his so-named "Japine papers."<sup>138</sup> This innovation was heralded by a considerable advertising fanfare.<sup>139</sup> The surface of Japine papers differed from the matte finish of all Willis's previous papers in displaying a semigloss or eggshell surface finish, with a distinct sheen that provided rich, deep shadows and an improved tonal gradation. The paper was initially available in a sepia color only,<sup>140</sup> but a "pure black" variety was soon marketed in 1908.<sup>141</sup> The technical manager of Willis's Platinotype Company, William H. Smith, recommended Japine papers to the Royal Photographic Society,<sup>142</sup> and Willis's long-term employee, Ernest A. Salt, described the Japine surface in these terms: "This is not an applied coating but is integral with the paper."<sup>143</sup> The same explanation was given by his contemporary Owen Wheeler: "[Japine] is not a coating, but exists as an integral part of the paper itself, giving maximum detail and shadow transparency."<sup>144</sup>

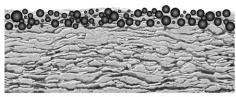
The question of the exact nature of this surface finish was raised again in modern times by the photograph conservator Lisa Barro, arising from her studies of 2002 in conserving the work of Paul Strand (1890–1976) on Japine papers.<sup>145</sup> Barro cites written evidence that Willis's Japine Platinotype papers may have been coated onto stock that had been partially parchmentized.<sup>146</sup> This is a process that typically involves a brief (3-10 seconds) treatment with strong (65-75%) sulfuric acid, followed by thorough washing and neutralizing with alkali.147 Barro's institution, the Metropolitan Museum of Art in New York (MMA), was later fortunate to acquire an unopened tin of Japine Platinotype for Sepia Tones, which stimulated the recent research to determine the nature of the surface and to aid the identification of prints of this type. The researchers at the MMA shared their specimen with the conservation scientists at the NGA, and both teams confirmed by a range of spectroscopic, analytical, and microscopical techniques that the parchmentized surface consisted of a smooth and lustrous "crust" of reprecipitated amorphous cellulose.<sup>148</sup> Infrared and Raman spectroscopy by MMA scientists showed the absence of waxes or proteins but the presence of an amorphousrather than the usual crystalline-form of cellulose on the surface of Japine.<sup>149</sup> At the NGA, GC-MS analysis was applied to the Japine sample and found essentially the same result as with the KK paper: the surface consists only of cellulose without any colloidal binders. Clarke and McCabe at the NGA succeeded in simulating the Japine surface by a parchmentization procedure applied to a suitable Crane & Company paper, and the surface was successfully printed on in platinum and palladium (see the essay by Karnes).<sup>150</sup> Photograph conservators are accustomed to distinguishing between three different

Year	Name of Paper	Main Characteristics
1879	Platinotype	Hot developer bath, neutral color
1885	Sepia Platinotype	Brown image caused by mercury salts
1887	Cold bath	Platinum salt in a cold developer; unstable
1892	Cold development	Platinum salt back in the sensitizer; no patent
1906	Sepia Japine Platinotype	Parchmentized paper surface, brown image
1908	Black Japine Platinotype	Parchmentized paper surface, neutral image
1913	Satista paper	Silver in excess added to platinum sensitizer
1916	Satoid paper	Silver-containing paper, brown image
1917	Japine Palladiotype	Palladium, parchmentized surface, brown image
1918	Matt Palladiotype	Palladium, matt surface, warm black image
1931	Warm Black Japine	Platinotype, with extra coating for Paul Strand

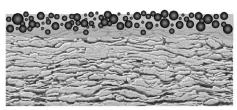
# Table 4 | Essential Types of Sensitized Paper from the Platinotype Company

69 Mike Ware, "The Technical History and Chemistry of Platinum and Palladium Printing" in *Platinum and Palladium Photographs: Technical History, Connoisseurship, and Preservation*, ed. Constance McCabe (Washington, D.C.: American Institute for Conservation of Historic and Artistic Works, 2017), 46–83.

Figure 18. Categories of photographic print laminar structure. Courtesy of Constance McCabe.



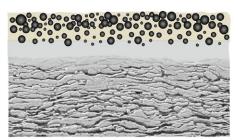
18a. One-layer print: plain, unmodified paper prints.



18b. One-layer print with modified surface: "Japine."



18c. Two-layer print: albumen or gelatin without baryta.



18d. Three-layer print: gelatin or collodion binder with baryta layer.

laminar structures for prints, but this research has added a fourth—previously unrecognized—category: "Single layer print with modified surface" (fig. 18). The essay by Alisha Chipman and Matthew L. Clarke shows how Japine papers played a very important part in the work of noted artists such as Paul Strand. The use of Japine as a designation for the surface sheen of the paper is complicated by the fact that it was offered in both matte and glossy surfaces.

# Willis's "Satista" and "Satoid" Papers

As a further economical measure to counter the soaring price of platinum, in 1913 Willis patented and introduced a compromise product that is reminiscent of his very first Platinotype papers of 1873-78: he used for image metal a mixture of platinum and silver, but predominantly the latter,<sup>151</sup> which made it substantially less expensive than Platinotype.<sup>152</sup> The name he chose for this product, "Satista," derives from the Latin satis for "sufficient."153 Unfortunately, in the long term, it was not. Although descriptive articles claimed that "the paper would give very fine black prints closely resembling Platinotype,"154 this product proved to be an uneasy hybrid: the process is effectively a platinum-catalyzed kallitype with ferric oxalate sensitizer, using the insoluble silver chloride, rather

than the soluble silver nitrate, because the latter would have caused the precipitation of unreactive silver chloroplatinite. Silver images from iron-based photochemistry like the kallitype are notorious for their propensity to fade, because any residual iron(III) can oxidize the image silver, especially in the presence of atmospheric moisture. Willis maintained that Satista prints were permanent, arguing on the rather self-contradictory grounds that, even if all the silver in the image faded, the remaining platinum could still be sufficient to retain all of the original image detail, and tests were reported of its resistance to fading.<sup>155</sup> It appears that Satista papers were made in two varieties: one to give a black image only, by room temperature development, and the other to furnish a brown image when developed hot (40–70°C). In his Satista patent of 1913, Willis indicated that a parchmentized paper was a possible substrate;<sup>156</sup> but he does not there use the word "Japine." However, the *BJP Almanac* stated that "of the two grades of Satista, black and sepia, both were coated on semi-matt hard-surfaced paper similar to Japine;"<sup>157</sup> and

in 1915 a visitor to the Platinotype Company's factory at Penge stated that Satista had indeed been coated on Japine paper hitherto.<sup>158</sup>

Later, in 1916, the Platinotype Company introduced a similar platinum-silver paper named "Satistoid," which was said to yield "deep rich brown tones" by room temperature development in proprietary "Satistoid" developing salts, which were also used at greater dilution for the clearing process, followed by a hypo bath.<sup>159</sup> The name of this paper appears to have soon become contracted to "Satoid,"<sup>160</sup> possibly to avoid confusion with "Satista."<sup>161</sup>

The window of opportunity to use Willis's Satista and Satoid papers was fortunately rather limited—they were launched in 1913 and 1916 respectively, and ceased to be advertised by 1929—so relatively few photographers employed them. However, the wartime shortage of Platinotype paper did induce some printers to turn to these alternatives, including the celebrated photographers Frederick Evans, Alfred Stieglitz, and Paul Strand. A few of Strand's most important works were printed on Satista c. 1916, and have since suffered significant image deterioration, including fading and discoloration of the midtones, problems that originally attracted the attention of conservator Barro in 2002,<sup>162</sup> and Constance McCabe, Christopher McGlinchey, Matthew L. Clarke, and Christopher A. Maines in 2015 (see technical highlight "Satista Prints and Fading"). Because of the relevance of the process to these important works by Strand and Stieglitz, research into Satista is still ongoing at the NGA and MMA, although no sensible practitioner today will make use of this chemically flawed and labor-intensive process.

#### The Platinotype Embargo in Britain

By 1916, platinum had acquired strategic status as the essential catalyst for manufacturing the vast quantity of nitrate explosives needed to prosecute the First World War (fig. 19). The British government consequently imposed an embargo on the use of platinum for any other purpose,<sup>163</sup> which was later exacerbated by the platinum famine in the West resulting from the revolution of 1917 in Russia, whence most of the supply had previously come. The British legislation effectively put a stop to Willis's manufacture of his Platinotype papers and their export to the United States 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

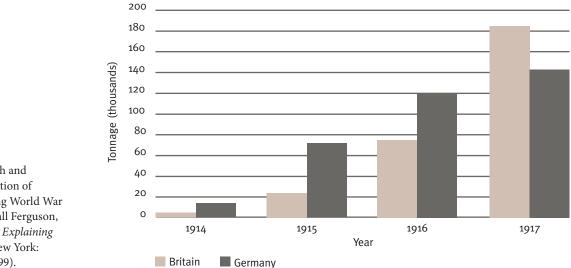


Figure 19. British and German production of explosives during World War I. Data from Niall Ferguson, *The Pity of War: Explaining World War I* (New York: Basic Books, 1999).

<sup>71</sup> Mike Ware, "The Technical History and Chemistry of Platinum and Palladium Printing" in *Platinum and Palladium Photographs: Technical History, Connoisseurship, and Preservation*, ed. Constance McCabe (Washington, D.C.: American Institute for Conservation of Historic and Artistic Works, 2017), 46–83.

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."<sup>164</sup>

Throughout the war years, issues of the authoritative annual *BJP Almanac* entirely omitted any mention of the Platinotype process from its editorial "Epitome of Progress," with no remarks even about its unavailability.<sup>165</sup> In 1917, 1918, 1919 the "Progress" section headed "Platinum Printing" carried only descriptions of Willis's Palladiotype paper (see below); there were no comments whatever on the dearth of platinum: the subject was evidently a sensitive one at the time.

By 1920, supplies of Platinotype paper had come back on stream,<sup>166</sup> but at such excessive prices that there was serious doubt if this medium of photography could be sustained: the *BJP* observed, "The question arises whether the process of platinum printing is not in danger of extinction."<sup>167</sup> In the United States the Women's National League for the Conservation of Platinum was patriotically founded by Mrs. Ellwood B. Spear in 1918<sup>168</sup> with the backing of the American Chemical Society.<sup>169</sup> American photographers were confronted with an ethical as well as a financial dilemma when selecting their print medium,<sup>170</sup> and serious consideration was given in the American photographic press to the alternatives to platinum, such as palladium and the iron-silver kallitype processes.<sup>171</sup> In 1918 the Platinotype Company resumed its advertising of Platinotype in the British photographic press, but now in the poignant context of World War I (fig. 20). There is a touching irony buried in this recommendation that "the photographs of your sons and brothers" should be immortalized in the same precious metal that could have been instrumental in their destruction as fighting men.

#### Willis's Palladiotype

In 1917 Willis responded to the challenge of the British platinum embargo with another innovation: his Palladiotype paper, using the closely related noble metal palladium, which had not yet found strategic industrial applications. There were precedents for printing processes in palladium: first by Charles J. Burnett (1856),<sup>172</sup> then by Willis himself (1878),<sup>173</sup> and Pizzighelli and Hübl (1882),<sup>174</sup> but palladium was not used as a substitute for platinum printing in the early days because the metal was even more scarce than platinum at the time, and the image was found to be more prone to "solarization" when

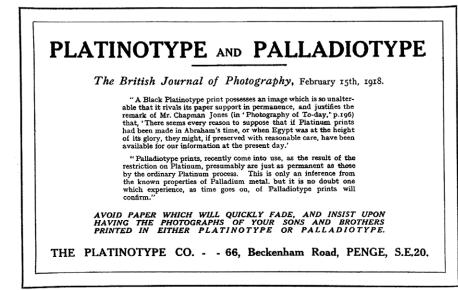


Figure 20. Platinotype Company advertisement for "Platinotype and Palladiotype." From *Photography* (February 27, 1918): xv.

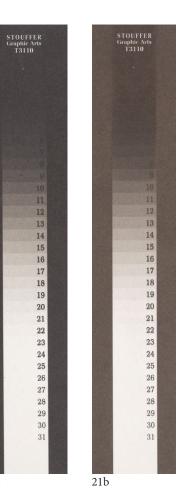
<sup>72</sup> Mike Ware, "The Technical History and Chemistry of Platinum and Palladium Printing" in *Platinum and Palladium Photographs: Technical History, Connoisseurship, and Preservation*, ed. Constance McCabe (Washington, D.C.: American Institute for Conservation of Historic and Artistic Works, 2017), 46–83.

Figure 21. Palladium steptablets printed identically on Weston Diploma Parchment paper, prepared by Mike Ware. Note the tonal reversal that occurs at the lower RH (21b), causing the D-Max to be both lighter and more brown than that of the more humid print (21a). 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 in the order of 1000× results in tonal reversal. Massive overexposure is not required to produce this effect in palladium and platinum prints. "Tonal reversal" is the term preferred to denote similar phenomena, such as solarization, bronzing, split-tone, or double-tone.

21a. Sensitized and preconditioned to 67% RH prior to exposure.

21b. Sensitized and preconditioned to 27% RH prior to exposure.

21a



heavily exposed, showing a reversal to brown tones in the shadows (fig. 21). However, by the 1890s, the use of palladium to tone silver prints became well established in order to make photoceramic images, which thereby gained the necessary resistance to kiln-firing under a glaze.<sup>175</sup>

The employment of a mixture of 20% palladium in a platinum sensitizer in order to impart sepia print tones was recommended in von Hübl's 1895 treatise,176 and echoed in English translation by E. J. Wall,<sup>177</sup> who later advocated mixed platinum-palladium sensitizers in his 1923 article on "The Iron Salts" in American Photography.<sup>178</sup> In view of these precedents, it is surprising that William Willis seems never to have adopted mixing an amount of palladium with his platinum to overcome some of the difficulties that arise with using the latter alone. The advantageous mixing of the two noble metals for image making did not become standard practice until the 1960s, when it was taken up by Irving Penn, as described in the essay by Vasilios Zatse and Constance McCabe.

The First World War soon enforced the adoption of palladium as a total substitute for platinum printing. The first hint of Willis's Palladiotype innovation came with an unexpected demonstration in January 1917 by William H. Smith of the Platinotype Company to a meeting of enthusiasts at the local Croydon Camera Club,<sup>179</sup> of which he was a prominent member. Without disclosing that it was actually palladium, he just introduced the product as a "brand new printing paper" and a "radically new departure."<sup>180</sup> It met with the general approval of the club members. On March 8, in a demonstration to the more august Camera Club of London, the same luminary revealed that it was, in fact, Palladiotype.<sup>181</sup> He showed that both developing and clearing of Palladiotypes were accomplished simply with baths of 5% potassium citrate solution acidified with 0.26% citric acid. The tendency of Palladiotype to solarize was acknowledged, and contrast enhancement by dichromate was also described. In recording the vote of thanks to the speaker it was remarked prophetically: "The introduction of this new printing process would be one of the landmarks of the history of photography."

Willis & Clements in the United States first advertised the paper in 1917 as "Palladiotype Sepia,"<sup>182</sup> but soon the commercial product was being described in England as "Sepia Japine Palladiotype paper,"<sup>183</sup> which was referred to in more familiar terms as "Sepia Vellum" in the United States. Willis & Clements also stamped its sample prints on the verso with "W & C Palladio,"<sup>184</sup> a label that may explain the use of the term in various sources, including Stieglitz's letters, as referred to in the essay by Greenough.

Following the Japine surface sepia paper, matte surface varieties of Palladiotype paper were advertised by Willis's Platinotype Company in March 1918 and publicly demonstrated once again by William H. Smith.<sup>185</sup> 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.<sup>186</sup> In 1921, Ernest Albert Salt, departmental manager, claimed that the company's Palladiotype papers had just undergone a very significant improvement,<sup>187</sup> and in 1922 the company proudly announced a further reduction in the prices of its Platinotype and Palladiotype papers.<sup>188</sup>

# Paul Anderson and the Clarence H. White School

Platinum printing became an important photographic medium in the United States thanks largely to the teaching 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 country dedicated to photography as fine art.<sup>189</sup> A valuable overview of the role of precious-metal printing in early twentieth-century American photography is provided by Constance McCabe,<sup>190</sup> who shows how several famous alumni of the White School became noted exponents of platinum printing. They owed their acquired skills to the fact that in the early years of 1914–18 Clarence White hired Paul Lewis Anderson, an electrical engineer, as an instructor on the faculty to teach the techniques of photography. Anderson had become an experienced advocate of platinum printing with his publications of 1913, in which he stated that it met all seven of his criteria for selecting a printing paper, as cited and discussed in the essay by Wagner: "permanence, repeatable printing, easy control and manipulation, modifiable image color and paper texture, and foremost, quality."<sup>191</sup>

Anderson published a handbook in 1917 based on his White School lectures, with an appendix that shows that he had already made a start 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.<sup>192</sup>

When the closure of the Platinotype Company in 1937 suddenly deprived fine-art photographers in the United States 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 practicing and republishing formulas in 1937-38. 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 United States], 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."193 Anderson's instructions for palladium printing continued to ignore the processing procedure recommended by Willis & Clements, as described below, and instead specified the same oxalate developer as was used for platinum 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. 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 (see the essay on Stieglitz by McCabe et al.). A connection between the two men during the years 1914-17 lay in the mutual acquaintance of Karl Struss (1886-1981), who shared a pho-

<sup>74</sup> Mike Ware, "The Technical History and Chemistry of Platinum and Palladium Printing" in *Platinum and Palladium Photographs: Technical History, Connoisseurship, and Preservation*, ed. Constance McCabe (Washington, D.C.: American Institute for Conservation of Historic and Artistic Works, 2017), 46–83.

tographic 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, *Camera Work*.<sup>194</sup>

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," as described in the essay by Clarke, "Characterization, Degradation, and Analysis of Platinum and Palladium Prints." Surprisingly, Schumpelt was granted a U.S. patent in 1941 for a palladium printing process,<sup>195</sup> although his specification contained nothing that had not previously been published by Anderson. The procedures for platinum printing recommended by Anderson, which he derived from Pizzighelli and Hübl, subsequently became standard practice in the United States, as evidenced by the reference works of Henney and Dudley (1939),<sup>196</sup> Wall and Jordan (1940),<sup>197</sup> Arnold Gassan (1977),<sup>198</sup> and William Crawford (1979),<sup>199</sup> and contemporary manuals such as the comprehensive handbook by Christopher James.<sup>200</sup>

#### Processing of Platinotype and Palladiotype

As noted above by Anderson, William Willis recommended quite different chemistry for processing these two kinds of paper. Platinotypes were customarily developed in neutral, or slightly acidic, potassium oxalate solution, the recommended strength being c. 25% w/v, but some workers preferred a solution nearly saturated at 33% w/v. Before 1892 the developer solution had to be 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.<sup>201</sup> After 1892, the preference shifted to Willis's new "cold development" papers, which were welcomed for their 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 potassium dihydrogen phosphate as well as potassium oxalate.<sup>202</sup>

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 molar, 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, and some workers employed much longer clearing times. Finally the print was washed in water for about 20–30 minutes.<sup>203</sup>

In contrast, for his Palladiotype papers, Willis recommended development in trisodium citrate solution (20% w/v) acidified with added citric acid (2% w/v); cleared in the same, 8× 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.<sup>204</sup> William Willis was a shrewd and observant chemist, painstaking in his perfection of process.<sup>205</sup> 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. However, as noted above, this point was not generally accepted in the United States, where practitioners of Palladiotype, encouraged by the examples of Alfred Stieglitz and Paul Anderson, tended to use the Platinotype developer of potassium oxalate that was already on their darkroom shelves rather than make up new solutions of sodium citrate.

The differing consequences of using oxalate and citrate developers for Palladiotypes have been tested and compared in recent research by Alice Carver-Kubik at GEM.<sup>206</sup> It was found in general that the oxalate developer solution gives slightly higher densities

and warmer image color in palladium prints, but it does tend to cause a perceptible chemical fog in the high values, which is worsened by humid conditions.<sup>207</sup> Carver-Kubik also tested the effects of adding mercury(II) salts—both to the palladium sensi-tizer and to the oxalate developer—finding that, contrary to the effect on platinum, the mercury(II) actually "cools" the palladium image to a more neutral tone. This result calls for an explanation of the analytical finding of mercury in a number of Palladio-types. It is possible that mercury was deliberately added to the developer to impart a cooler hue to the warm palladium image. However, the mercury may owe its presence to the practitioners' reuse of oxalate developer, which had previously been employed for sepia Platinotype, and thereby accumulated mercury(II) salts.

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, and it can be partially "cleared" by the hydrochloric acid—a case of two errors in processing being somewhat self-canceling!

It is important to note that Willis made every reasonable attempt to provide clear chemical working instructions on how to prepare a platinum or palladium print that would be expected to last. Different chemicals for each process were published and marketed by both the Platinotype Company and Willis & Clements. Practitioners of these processes, however, may not have heeded these specific recommendations, and incorrectly assumed that the chemicals for platinum might be used for palladium. This misapprehension may be responsible for the significant number of stained and faded prints found in collections.

# **Chemical Comparison of Platinum and Palladium**

Although the platinum atom has many more electrons orbiting around its much heavier nucleus than the palladium atom, the two atoms are actually about the same size.<sup>208</sup> Hence platinum is more dense and less reactive than palladium, as can be seen in the data of table 5. A good print can be obtained from a mixture of the two metals because they form a continuous solid solution over the entire range of composition at room temperature, as is apparent from the binary phase diagram for the platinum-palladium alloy. Table 6 compares the working characteristics of platinum with those of palladium, the latter being generally easier to print and working well on a wider range of paper supports than platinum. Its lower cost and other user-friendly characteristics account

# Table 5 | Comparison of Atomic Properties of Palladium and Platinum

Palladium Platinu	ım Units
ber 46 78	
mic mass 106.4 195.1	
ius 137.3 138.5	pm
12.0 21.5	g/cc
2+ 78 74	pm
4+ 75.5 76.5	pm
ius     106.4     195.1       ius     137.3     138.5       12.0     21.5       2+     78     74	g/cc pm

#### Table 6 | Palladiotype versus Platinotype

Palladiotype	Platinotype
Faster, more reactive	Slower to form metal
Warm brown color	Neutral gray color
Very long exposure scale	Long exposure scale
Softer gradation in highs	More contrast in highs
Attacked by HCl + air	Impervious to HCl + air
Tolerant of impurities	Inhibited by impurities
Easier chemistry	Harder to prepare
Expensive	Very expensive

for the popular employment of palladium in preference to platinum, which has opened a new chapter in noble metal printing, carrying it into the present-day practice, where palladium now predominates.

It is important for contemporary practitioners to acknowledge that palladium bears the same relation to platinum as silver does to gold, as may be seen from the periodic table of the elements. Now, metalsmiths and jewelers dealing in gold and silver are obliged to be scrupulous in their descriptions: they work to a system of hallmarks regulated by assay offices. By analogy, in modern precious-metal printing, it has become usual to mix palladium and platinum; the author would therefore appeal to all platinum-palladium printers to be scrupulous, too, in describing their print media. This is not so much an issue of the financial worth of the actual metal in the prints, or even the relative difficulty in making the print, but rather because inaccuracy in their description now could store up problems for the future conservation of such artworks.

# Later History and Closure of the Platinotype Company

William Willis died in 1923.<sup>209</sup> Control of the company then passed to his younger brother, John Willis, as sole proprietor, who promptly incorporated it as a private limited company, registered on January 14, 1924, with a nominal share capital of £12,000. Charles Robinson was appointed as managing director and, as director and secretary, Alfred Willis Clemes, a first cousin of William Willis, once removed, who was a mining engineer and Rhodes Scholar from the branch of the family that had emigrated to Tasmania, c. 1886.<sup>210</sup> 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 dissolved on August 30, 1932, at a general meeting held by Charles Robinson, the current chairman.<sup>211</sup> Ownership having been transferred in November 1931 to the directors, Robinson and Clemes, the once more delimited Platinotype Company remained in business as the only manufacturer of platinum papers in the world. Furthermore, in 1931 Willis & Clements agency for Platinotype Company papers was terminated, and clients in the United States were thereafter supplied directly from the company in London. In the summer of 1937, the coating plant was shut down on June 20, and the last of the company's stock of Warm Black Japine Platinotype paper, "W.B.J.," which had been specially double-coated at the behest of Paul Strand, as described in the essay by Chipman and Clarke, was sold to Hollywood photographer Ned Scott (1907-1964).<sup>212</sup> Seeking information about sensitizing their own papers, Scott and Strand engaged in a final correspondence with the Platinotype Company, which brought a letter from Charles Robinson to Scott with a discouraging observation that now stands as a telling epitaph for 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."213

The Platinotype Company was then finally dissolved. Its ultimate demise can be attributed to the limitation suffered by all the siderotype processes: the near-necessity for printing by contact, using a same-size negative to permit a sufficient throughput of light. Enlarging onto platinotype paper by projection called for very lengthy exposures with specialized light sources and optical systems; these were not commonly possessed by the amateur. In the 1930s the growing popularity of miniature cameras recording negatives on roll film demanded enlargement, but convenient exposure times for printing by projection required a sensitivity that only developed-silver photography could supply, thus guaranteeing its commercial dominance for the rest of the twentieth century.

77 Mike Ware, "The Technical History and Chemistry of Platinum and Palladium Printing" in Platinum and Palladium Photographs: Technical History, Connoisseurship, and Preservation, ed. Constance McCabe (Washington, D.C.: American Institute for Conservation of Historic and Artistic Works, 2017), 46–83.

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2. Sir John F. W. Herschel, "On the Action of Light in determining the Precipitation of Muriate of Platinum by Lime-water," *London, Edinburgh, and Dublin Philosophical Magazine* 1 (July 1832): 58–60. The substance is today more correctly described as calcium hexahydroxyplatinate(IV).

3. Larry J. Schaaf. *Out of the Shadows: Herschel, Talbot and the Invention of Photography* (New Haven: Yale University Press, 1992), and references cited therein.

4. 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.

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6. Mike Ware, *Cyanotype: the history, science and art of photographic printing in Prussian blue* (London: Science Museum, 1999), 24–27, and references cited therein. See also Mike Ware, "Herschel's Cyanotype: Invention or Discovery?" *History of Photography* 22, no. 4 (Winter 1998): 371–79.

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28. Luis Nadeau, *History and Practice of Platinum Printing*, 3rd ed. (Fredericton, New Brunswick: Atelier Luis Nadeau, 1994). This text reproduces five of Willis's six patents.

29. William Willis, "A New Process of Photo-chemical Printing in Metallic Platinum," *British Journal of Photography* 25 (August 23, 1878): 400; *idem*, "Notes on the Platinotype Process," *British Journal of Photography* 26 (February 14, 1879): 73–74.

30. Christie's, South Kensington, *19th and 20th Century Photo-graphs*," sale cat., London, April 21, 1988, 38, item 107.

31. William Mansfield worked as a chemist for the Platinotype Company.

32. William Willis 1878, 400. Ref. 29.

33. William Willis, "Notes on the Platinotype Process," *Photographic Journal*, n.s. 3, no. 3 (December 13, 1878): 32–34 (old series vol. 19).

34. William Willis, "Notes on the Platinotype Process," *British Journal of Photography* 25 (December 20, 1878): 605–8.

35. Although they have today acquired generic significance, the names "Platinotype" and "Palladiotype" (capitalized thus) were originally the registered trade names for the products of Willis's Platino-type Company. In this account they will be so distinguished from all other platinum and palladium printing papers either manufactured by other companies or handmade by the printer.

36. The major histories of photography give 1879 as the year of the establishment of the Platinotype Company, but its official headed notepaper states 1878, and this year is confirmed by the legend embossed on the lids of some Platinotype paper tims: "Established 1878."

37. James Young, "The Platinotype Printing Process," *British Journal of Photography* 27 (January 16, 1880): 29–30.

38. 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.

39. At 66 Beckenham Road, Penge, later to become 66 High Street, Penge, London SE 20.

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