Photographers have always been motivated to manipulate chemistry and production of prints to achieve specific aesthetic goals. By the late nineteenth and early twentieth centuries, artists routinely toned silver prints with platinum salts to attain the platinum effects they desired more economically than by printing in platinotype.¹ Toning with gold and platinum was believed to impart even greater permanence than by toning with either gold or platinum alone, and combining these toning agents increased the range of colors realized, with hues running the gamut from reddish-brown to purple-black (fig. 1).²

As early as 1856, Ernest de Caranza (1817–1868) wrote about his experiments using platinum as a toning agent, suggesting the use of platinum(IV) chloride in hydrochloric acid as the toning solution.³ His formula was not widely adopted because it caused a dramatic loss in image density and only a slight color shift.⁴ The practice of toning silver prints with platinum did not become effective or commonplace until after the 1870s, when William Willis Jr. (1841–1923) of the Platinotype Company made the compound potassium tetrachloroplatinate(II) commonly available.⁵ Lyonel Clark was able to use this platinum salt with more success than earlier experimenters, and he wrote an influential treatise on platinum toning, which was reissued in several subsequent editions.⁶ Clark’s success was largely due to the ability of potassium tetrachloroplatinate(II) to reduce to metallic platinum more easily than platinum(IV) chloride, while replacing fewer silver particles. Thus the density of the silver image was not as significantly diminished by the toning process.⁷

Clark published and displayed the results of his experiments shortly after Willis presented a lecture on platinum printing to the Camera Club of London in 1888.⁸ In 1890, Alfred Stieglitz published two recipes for platinum toning of aristotype printing-out prints (modern equivalents in parentheses):⁹

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**oxalate-phosphate recipe**
Mix 6 parts of solution A with 1 part of solution B to create a bath for toning:

```plaintext
solution A
- potassium oxalate 3½ ounces (99 g)
- potassium phosphate 1¼ ounces (50 g)
- distilled water 1 quart (0.95 L)

solution B
- potassio-platinous chloride 15 grains (0.97 g)
- distilled water 6 drams (22 mL)
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**nitric acid recipe**

```plaintext
- potassium-platinous chloride 15 grains (0.97 g)
- distilled water 1 quart (0.95 L)
- nitric acid, concentrated 25 minims (1.5 mL)
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Figure 1. George Nussbaumer, *Studio Work*, c. 1895. Platinum-and-gold-toned silver print, image 14 × 9.6 cm. Sample photograph printed on American Aristotype Company’s Aristo-Platino paper. From [George W. Gilson], “Studio Work,” *Canadian Photographic Journal Illustrated* 4 (October 1895): 253. Aristo-Platino was one of the most widely used matte collodio-chloride papers for platinum and gold toning.
Clark described Stieglitz's oxalate-phosphate recipe as being very similar to the Platinotype Company's "ordinary," or platinum-in-the-bath, developing solution.¹⁰

From the 1890s to the 1920s, platinum toning was carried out on several silver printing-out processes, including plain salted paper, albumen, collodion, and gelatin papers, as well as gelatin silver developing-out papers (fig. 2).¹¹ In 1898, the *Photographic News* noted that "any gelatino or collodio-chloride paper, whether matt or glossy, may be toned with platinum."¹² In the following year, however, John A. Tennant, editor of the *Photo-Miniature*, wrote that platinum toning in the United States was carried out "almost exclusively" on matte-collodion printing-out papers, while in England it was in limited use on gelatin chloride printing-out papers and plain salted paper prints.¹³ While both silver bromide and chloro-bromide papers are mentioned in the contemporary literature as suitable for toning, silver-chloride papers appear to have been the most commonly used because their images changed most noticeably during the process.¹⁴

The entire October issue of the *Photo-Miniature* of 1899 was dedicated to the Platinotype and referred to Clark's platinum toning manual for the preparation of plain papers for platinum toning.¹⁵ Clemon's Salted Paper is specifically mentioned as an excellent presalted paper for platinum toning, being a "reliable paper, obtainable commercially."¹⁶ Paul Hasluck wrote that toning with platinum was "little used for the glossy varieties" of printing-out or collodio-chloride papers because the tones produced were better for matte surfaces.¹⁷ Some silver printing-out papers were specifically marketed for toning, such as the Aristotype Company's Aristo-Platino, which was one of the best-known matte collodio-chloride papers for platinum and gold toning (fig. 3).¹⁸

As with other toning processes, platinum toning required an experienced eye and additional processing steps before fixing and washing. Most manuals and practitioners recommended overexposing the prints because the image density would ultimately decrease with the toning.¹⁹ An initial rinse in water removed the bulk of the unexposed silver salts, thus helping to preserve the precious-metal toning bath.²⁰ Furthermore, adding a little salt water during this rinsing step was sometimes recommended to assist in removing unexposed silver salts from the print.²¹ Immersing the print in the toning bath started the replacement reaction of platinum for silver. The print was removed when the desired color was reached, with the

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Figure 4. Caroline Minchew, *Platinum Accoutrements*, 2016. Contact prints from 8 × 10 inch negative and corresponding XRF spectra. All prints courtesy National Gallery of Art, Photograph Conservation Study Collection. These four prints were created using historically accurate processes from the same negative. Their varying tonalities and density ranges highlight the difficulty of differentiating the printing process based on visual examination alone. The corresponding XRF difference spectra clearly show the metals that compose the image in each of the prints: the salted paper print image is composed solely of silver; the platinum print is composed of platinum, while the Satista print and platinum-toned silver print contain both metals, complicating their identification.
understanding that the final image hue after drying would be slightly different. After toning, the print was washed in a bath of mildly alkaline water, sometimes rinsed further, fixed in sodium thiosulfate, and washed again.22

Toning baths with stronger concentrations of acid or platinum salts resulted in blacker tones, while weaker concentrations of acid or platinum favored sepia and brown tones.23 The duration of toning also influenced the final appearance. For example, weaker baths toned more slowly and provided the practitioner with more control. Thus the print could be removed from the bath while still brown in tone or left in the bath longer to achieve a more neutral appearance.24 Many variations of platinum-toning recipes were used, including ones that incorporated only platinum, combined platinum and gold in a single bath, or utilized a single gold bath followed by a platinum bath.25 By 1910, the standard method for toning collodio-chloride papers was to first use a gold bath followed by a platinum bath, with the length of toning in gold influencing the final appearance. For example, weaker baths toned more slowly and provided the practitioner with more control. Thus the print could be removed from the bath while still brown in tone or left in the bath longer to achieve a more neutral appearance.26

Palladium salts were occasionally discussed for toning silver prints, but the practice never gained the same popularity as toning with platinum. Despite brief mentions of palladium toning as early as 1859, Frank P. Perkins’s 1891 article on the use of palladous chloride for the toning of silver prints appears to be one of the few published references for this process.27 Palladium was generally thought to impart a browner color than platinum, producing a photograph tending toward sepia rather than black.28

Determining which specific process was used to create these prints is impossible by visual examination alone; toned silver prints vary widely in color, can be matte or glossy, and can have a variety of binders, or no binder at all. X-ray fluorescence spectrometry (XRF) is helpful in identifying a print’s metallic components, including silver, platinum, and gold. While the presence of these metals may be indicative of a platinum-and-gold-toned silver print, some platinum prints may have been intensified with silver or gold. Alternatively, the photograph could be printed on one of numerous commercially available papers in which the image is composed of silver and platinum.29 A photographer may have chosen one of these methods for the sake of economy or as a means of achieving a specific aesthetic. The relationship between process and appearance may have broader implications for the deterioration and stability of these prints, a topic of research that is still being elucidated.

Modern simulacra of different historic photographic printing processes illustrate how challenging it can be to differentiate one process from another.30 Further, XRF data alone may not provide sufficient information to determine the processes used to create the prints (fig. 4).31 Only by combining careful examination, analysis, and an understanding of the history of the photograph may the material nature of a print be revealed. Even with this information, the exact materials and methods used to produce historic prints may remain a mystery unless the photographer’s accompanying documentation is preserved along with the photograph.

Notes
2. Leeson 1893, 55; Wall 1897, 349; “Our Consulting Room: Toning” 1898; “Our Consulting Room: Platinum Toning” 1898a; Clark 1901, 21; “Answers to Correspondents” 1910; Smee 1914b, 440; Eder and Wentzel 1928, 64–66; Reilly 1980, 81; Hofmann and Schatal 2003, 86. XRF analysis of the image depicted in figure 1 detected silver, platinum, and gold in the high-density image areas. Lynn Brostoff, analysis report, October 19, 2016, Preservation Research and Testing Division, Library of Congress.
3. “Assemblée générale de la société” 1856, 82; de Caranza 1856, 14. Platinum(IV) chloride was also known as chloridin of platinum or platinic chloride.
4. Wall 1900, 221.
5. Clark 1901, 13; Jones 1904, 441. Potassium tetrachloroplatinate(II) was also known as potassium chloroplatinate, potassio-platinous chloride, and platinochlorine.
6. Clark 1890; Clark 1892; Clark 1895; Clark 1897; Clark 1901.
8. Clark 1901, 16.
9. Stieglitz 1890, 120–21; Gunther 1889, 331.
10. Clark 1901, 81; Woodbury 1891, 36; Wall 1897, 349; Reilly 1980, 81.
16. Clark 1901, 40–71; see also [Tennant] 1899, 353.
17. Hasluck 1905, 248.
18. [Tennant] 1907, 266.
19. [Tennant] 1899, 353; Clark 1901, 23; Jarman 1905, 707; Smee 1914a, 328.
22. Harrison 1891, 197; Leeson 1893, 56; Wall 1897, 350; “Platinum Toning” 1898; Clark 1901, 24–29; Jarman 1905, 707.
23. Clark 1901, 25–29; Hoppe et al. 1911, 204; Wall 1897, 350; Leeson 1893, 56; Hasluck 1905, 249–51.
24. Leeson 1893, 56; Clark 1901, 28; Hoppe et al. 1911, 204.
26. Fell 1897, 294; [Tennant] 1910, 553; “Gelatine P.O.P” 1914, 848; Eder and Wentzel 1928, 68; Pénichon 1999, 137.
27. Gwenthillian 1859; Perkins 1891.
30. All the prints were made at the National Gallery of Art Photograph Conservation Department. The salted paper print was created following the recipe suggested by Lyelon Clark (Clark 1901); the platinum-toned salted paper print was created using the same recipe and toned using Steiglitz’s nitric acid recipe (Steiglitz 1890); the Satista (silver-platinum) print was created following William Willis 1913 patent (Willis 1913), with thanks to Lisa Barro for her practical advice and guidance; and the platinum print (shown on the jacket of this volume) was created following the traditional platinum print recipes with the guidance of Mike Ware and as described by Caroline Minchew, “A Step-by-Step Guide to Platinum and Palladium Printing;” in this volume.
31. XRF spectra were acquired using a RönTec ArtTax µ-XRF equipped with a Rh anode x-ray tube operating at 50 kV and 300 µA. The unfiltered Rh x-rays were directed through a capillary optics lens. Spectra were accumulated over 300 s live time. Spectra were processed using the subtraction and smoothing functions in the Bruker Artax Spectra (Version 7.2.5.0) software package. The XRF difference spectra (D-Max minus D-Min) are the result of subtracting a spectrum collected at minimum image density (D-Min) from one at maximum density (D-Max) to isolate the contribution from the image material.

References


"Our Consulting Room: Platinum Toning" 1898a "Our Consulting Room: Platinum Toning." Photographic News 42, no. 130 (June 24, 1898): 408.

"Our Consulting Room: Platinum Toning" 1898b "Our Consulting Room: Platinum Toning." Photographic News 42, no. 143 (September 23, 1898): 615.

"Our Consulting Room: Toning" 1898 "Our Consulting Room: Toning." Photographic News 42, no. 128 (June 10, 1898): 374.


