102   Matthew L. Clarke, "Characterization, Degradation, and Analysis of Platinum and Palladium Prints," 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), 102–115.

Characterization, Degradation, and Analysis of Platinum and Palladium Prints

Matthew L. Clarke

This volume fully illustrates that there are many ways to produce a platinum or palladium print. Much has been discussed about the "traditional" platinum print in particular, and the methods used to investigate platinum and palladium prints, both old and new, are similar. This essay will guide the reader through some of the physical attributes of the prints, such as how much platinum image metal is present, the amount of residual processing chemicals that may remain within the paper, what toning elements may be present, and, most important for conservation, how these prints may change over time. Prints may be characterized by analyzing naturally aged historic prints and preparing new prints using well-controlled conditions. These methods are explored, and some of the discoveries are discussed.

The Appearance and Structure of a Print

Before delving into the properties of platinum and palladium prints, it is beneficial to consider how a print is made (see appendix). Mike Ware has elegantly described the chemistry of the traditional printing process.[1] During this production process many factors must be taken into account, each of which has an impact on the final print. The choices include selection of a paper base and its sizing, the iron salt, the platinum or palladium salt and any toning metals, the humidity at which the sensitized paper is exposed, the clearing agents, and the washing conditions. Postprocessing treatments and finishing techniques, such as coating, also have an impact. All can influence the final appearance of a print and its life expectancy.

The Appearance of a Print

Examination of a large number of historic and modern prints opens our eyes to the wide variety of appearances possible in platinum and palladium printing. However, correlating a print's appearance with the conditions under which it was created is impossible unless these specific conditions were recorded, and they almost never were. Therefore, researchers in the Photograph Conservation and Scientific Research Departments at the National Gallery of Art and project collaborators found it beneficial to create a large set of platinum and palladium prints under controlled, select conditions in order to directly observe how different variables impact the prints' appearance and predicted longevity. These custom-made prints, or simulacra, were subjected to accelerated aging tests and stain reduction treatments (fig. 1). Details for the printing materials and methods are found in the appendix at the end of this essay.

The value of creating such a sample set can be readily grasped by examining the many processes side-by-side, such as the small group of prints in figure 2. For example, several mechanisms may be employed to produce prints that exhibit warmer tones than are typically associated with platinum prints. These include the use of a hot developer, the lowering of moisture content of the paper immediately prior to exposure, and the addition of mercury to the sensitizer or developer during the printing process (fig. 3). Indeed, the large variation in printed tones achievable was noted in the period literature

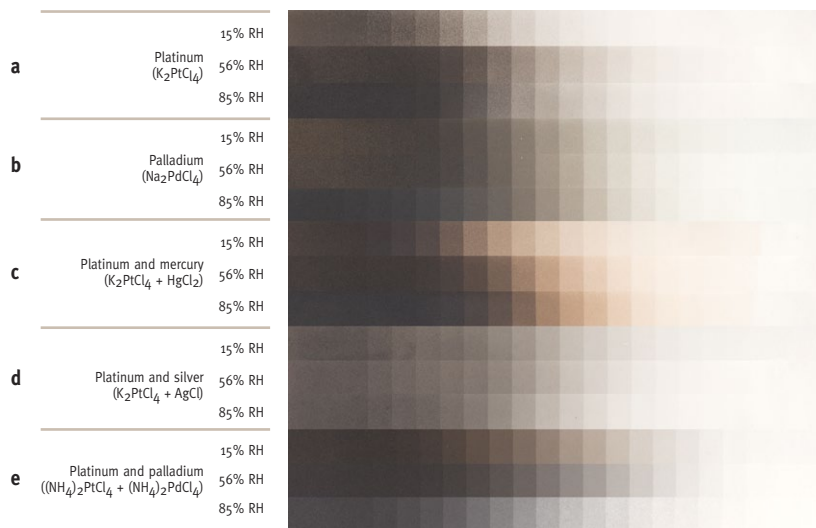Figure 1. Step-tablets of platinum and palladium prints prepared at the National Gallery of Art.

Figure 2. Print-processing variables and associated step-tablets prepared at the National Gallery of Art. Images are cropped to aid visualization. The relative humidity listed is for the paper during exposure. The form of metal salt is listed in parentheses. The ammonium process used ammonium ferric oxalate in the sensitizer (e), while all others used ferric oxalate (a–d).

a — Platinum (K_2PtCl_4) — 15% RH / 56% RH / 85% RH
b — Palladium (Na_2PdCl_4) — 15% RH / 56% RH / 85% RH
c — Platinum and mercury ($K_2PtCl_4 + HgCl_2$) — 15% RH / 56% RH / 85% RH
d — Platinum and silver ($K_2PtCl_4 + AgCl$) — 15% RH / 56% RH / 85% RH
e — Platinum and palladium (($NH_4)_2PtCl_4 + (NH_4)_2PdCl_4$) — 15% RH / 56% RH / 85% RH
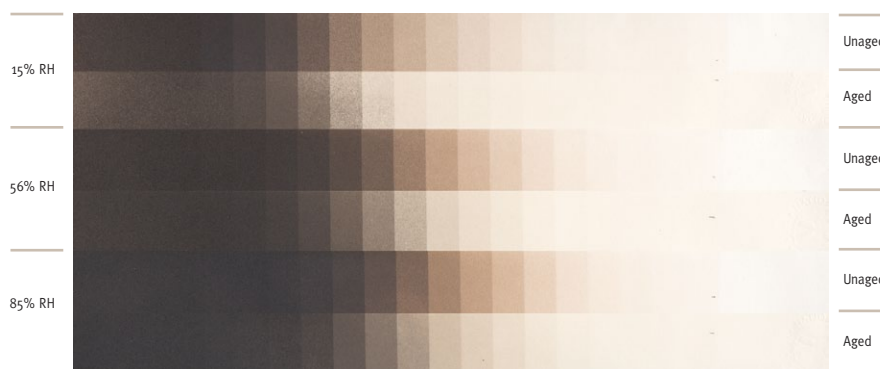

Figure 3. Platinum print step-tablets processed with mercury in the developer prepared at the National Gallery of Art. After sensitization, the sheet was split into three sections and equilibrated to three humidity levels. All three prints were then exposed together and processed identically. After the prints were dry, each section was split and one half was subjected to accelerated aging.

15% RH — Unaged / Aged
56% RH — Unaged / Aged
85% RH — Unaged / Aged

Figure 4. Table published in 1901 that lists different tones obtainable in platinum prints by the selection of a grade of Platinotype Company paper and with alterations to the developer composition (additives such as mercury or citric acid) and to the temperature. From "Tones on Platinum Paper," *Photo-Beacon* 13 (April 1901): 128.

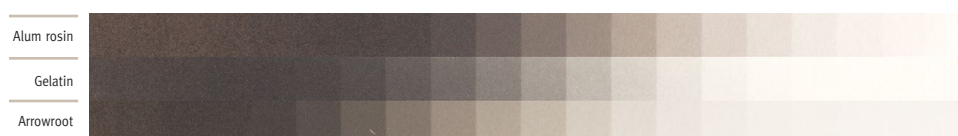| No.	Paper.	Potassium Phosphate.	Potassium Oxalate.	Mercury Bichloride.	Citric Acid.	Water.	Temperature of Developer.	Result.
1	AA	½ ounce	½ ounce			5 ounces	Warm, 70°	Warm black.
2	AA	½ "	½ "			5 "	Hot, 170°	Warmer black.
3	AA	½ "	½ "	3 grains		5 "	Hot	Brown black.
4	CC	½ "	1 "	30 "		5 "	"	Cold brown.
5	CC		1 "	30 "		10 "	"	Warm brown.
6	AA	¼ ounce	½ "	30 "	10 grains	10 "	"	Cold sepia.
7	AA		1 "	Abnormal quantity		10 "	"	Brick red.
8	CC	Company's D salts One ounce		30 Grains		1 pint	"	Rich brown.
9	CC	Company's D salts Two ounces		30 "		1 "	"	Sepia.
10	RS	½ ounce	1 ounce	3 "	10 grains	5 ounces	"	Warm brown.
11	RS	½ "	½ "			5 "	Warm	Rich brown.
12	RS	½ "	½ "			5 "	Hot	Purple brown.
13	RS	½ "	½ "	30 grains		5 "	"	Sepia.
14	RS	½ "	1 "	30 "		5 "	"	Warm sepia.

Alum rosin
Gelatin
Arrowroot

Figure 5. Palladium print step-tablets processed on cotton paper prepared at the National Gallery of Art. The raw paper stock contained alum rosin and starch sizing. It was then used as is or surface-sized with gelatin or arrowroot starch. The final prints show a difference in tone, with the alum rosin and starch-sized papers giving warmer tones than the gelatin.
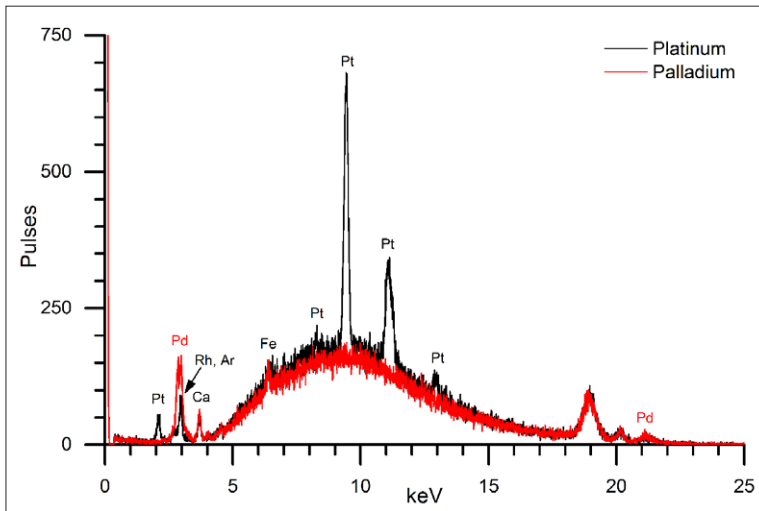
Figure 6. XRF spectra of platinum and palladium prints prepared on a 100% cotton paper.

als has been well described in the literature.[3] Examples of XRF spectra acquired from areas of high image density on platinum and palladium prints are shown in figure 6.[4]

While the metals forming the image are readily identified and measured by techniques such as XRF, it is exceedingly difficult to determine their specifics. For example, iron salts might be identified, but which iron salts? To distinguish among iron salts, the most appropriate common noninvasive analytical method would be infrared spectroscopy (i.e., attenuated total internal reflectance–Fourier transform infrared spectroscopy, ATR-FTIR). Even this technique, however, would not likely find the very small traces of minute materials related to the sensitizer left in the paper.[5]

The Structure of a Print

Photoreduction and reaction of the iron salts with the platinum or palladium salts result in the deposition of these precious metals onto and within the support, usually a high-quality paper. Examination of a palladium print by backscattered scanning electron microscopy (BS-SEM) shows the formation of these particles occurs near the surface of the paper, typically up to 10–20 micrometers (µm) deep, a depth that corresponds to the top layer or two of paper fibers (fig. 7).[6] The depth of penetration of the initial

(fig. 4). Switching from platinum to palladium salts can sometimes also yield warmer tones. Even changing the sizing of the paper can alter the final appearance. Palladium prints produced on gelatin-sized paper give cooler tones than those printed on starch-sized paper (fig. 5).

The tone of a print is related to the process, but with so many paths available to achieve a given tone, it is impossible to classify prints by eye alone. Identification is best performed by instrumental analytical techniques that allow many similar processes to be distinguished. Platinum, palladium, platinum-silver (e.g., Satista, platinum-toned silver prints), iron-silver (e.g., kallitype), and even photogravure may exhibit a similar palette of image hues, from blue-black to sepia, but they are readily differentiated by their elemental composition.[2] This can be determined noninvasively through nondestructive x-ray fluorescence (XRF) analysis. The use of XRF on photographic materi-

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Figure 7. BS-SEM image of a cross section of a palladium print. The lighter color near the top of the section indicates the presence of more electron dense elements. Scale bar = 100 µm.
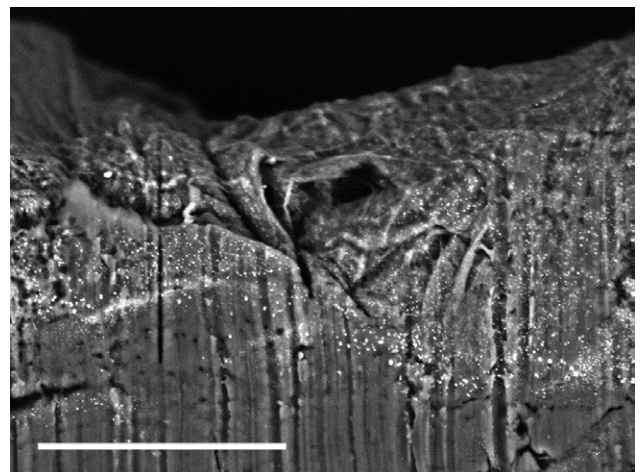
7a

7a. Further magnification of the cross section reveals the presence of palladium particulates, primarily within 10–20 µm of the paper surface. Scale bar = 25 µm.

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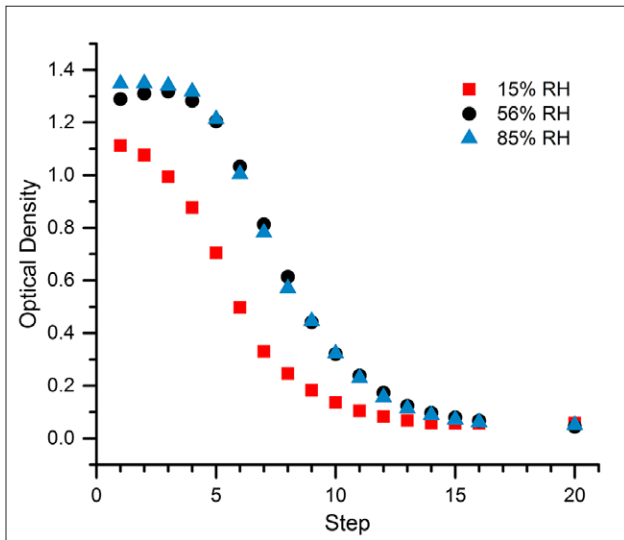
Figure 8. Graph exploring the optical densities of platinum step-tablets (shown in fig. 2) and the influence of humidity. It demonstrates that the printed image density increases for each step of the tablet for the platinum print. Higher humidity produces prints with overall greater image density and higher dynamic range. Step 20 corresponds to an unsensitized region of the paper. Palladium prints are much less affected by humidity.
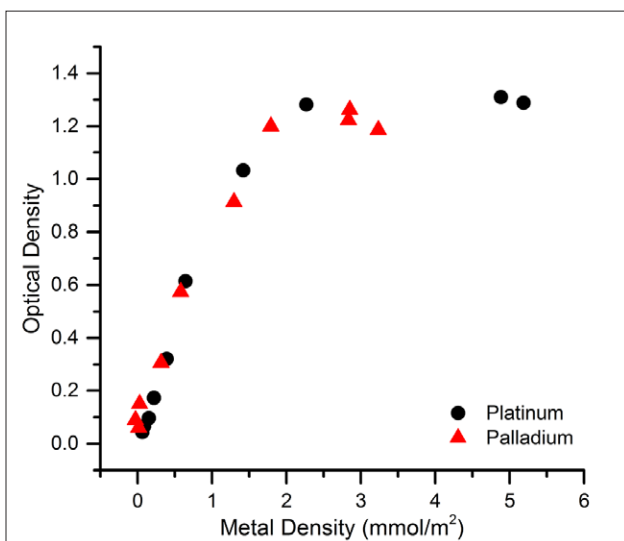

Figure 9. Graph exploring the printed metal as it relates to optical density. The amount of printed metal required to create a given optical density in each step of platinum and palladium step-tablets was measured by optical and XRF measurements. This graph shows that the relationship between the molar density of the printed precious metal and the observed print density was the same for both platinum and palladium. As palladium is nearly half the molar mass of platinum, less precious metal (by weight) is required to achieve the same image density.

sensitizing solutions into the paper base, the moisture content during exposure, the temperature of the developer, and many other factors can influence how and where these small metal particles form. The depth within the paper to which these particles print out during exposure and the overall visual appearance of the print can be influenced by

the properties of the paper base. For example, the Japine printing papers sold by the Platinotype Company were prepared on chemically modified cellulose that gave a glossier appearance and confined the sensitizing solutions to a shallower depth.[7] Each factor changes the size, shape, and distribution of the particles deposited and hence influences the density range, graininess, and tone of the final print. The metal image particles are on the scale of nanometers, and it is these tiny particles that are responsible for the hue and density of the perceived photographic image.[8]

The moisture content of the sensitized paper during exposure has a significant impact on the tonal range and appearance of the print. Humid paper gives neutral-toned prints, and dry paper gives warm-toned prints. Further, different printing conditions influence the density of the print, which can be measured and compared. Platinum metals deposit more readily when the sensitized paper is equilibrated to a high humidity level just prior to exposure. When exposed identically, a sensitized paper equilibrated to 85% RH produces a platinum print with deeper blacks (more metal and of neutral appearance) and with an overall wider contrast range than a print equilibrated to 15% RH, which produces a platinum print more sepia

Figure 10. Paul L. Anderson's 1923 description of sensitizing solutions. Stock solutions are prepared and mixed according to the desired level of contrast. Greater contrast is achieved by the increased amount of potassium chlorate in the final mixture. From Paul L. Anderson, *The Techniques of Pictorial Photography* (Philadelphia: J. B. Lippincott, 1923), 197, 199.

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Figure 11. Advertisements for chemical supplies marketed to the platinum and palladium community in 1940.

11a. Baker & Company advertisement for "Palladium Printing," *American Annual of Photography* 54 (1940): adv. 56.

11b. Paragon Testing Laboratories advertisement for "Paragon Palladium Paper," *Photo Technique* 2 (March 1940): 57.

PALLADIUM PRINTING
EXTRAORDINARY CONTRAST AND TONE CONTROL

PALLADIUM printing is a new and fascinating field for the photographic enthusiast. It gives you contrast and tone control to an extent exceeded only by Bromoil. The prints have unusual depth. Scale is three to four times as long as the longest scale portrait paper. Let us tell you about the Baker Sensitizing Set, which makes palladium printing practical, simple and easy.

BAKER & CO., INC.
113 ASTOR STREET   NEWARK, N. J.

11a

Paragon Palladium Paper

Prints made with Paragon Palladium Paper are absolutely permanent and cannot fade because the image does not lie upon the surface but actually penetrates and becomes part of the paper. Photographs may be exposed to direct sunlight without ill effect. Paragon Palladium paper has a scale which is three to four times longer than that of even the longest scale portrait paper. No darkroom is needed for developing. Write for complete information and prices.

PARAGON TESTING LABORATORIES
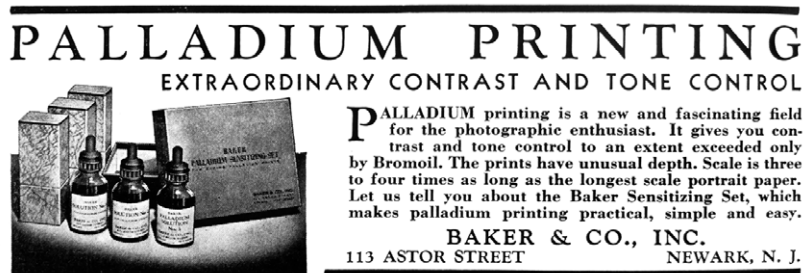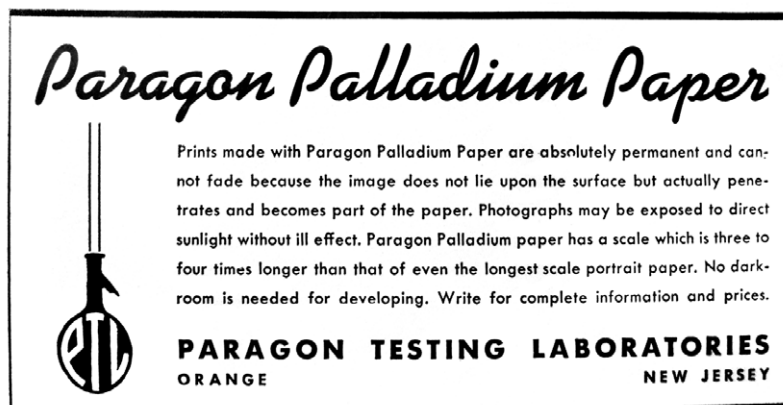ORANGE   NEW JERSEY

11b

in hue (fig. 8). A change in the image tone is the most noticeable effect of humidity on the palladium printing process (see fig. 2), with drier prints yielding browner tones. The quantity of metal deposited determines the overall perceived image density (optical density).[9] When platinum and palladium prints are prepared in the same manner, they exhibit a nearly identical relationship between the molar density of the printed precious metals and the optical density (fig. 9). Simply stated, it takes the same number of platinum or palladium atoms per unit projected area to achieve the same image optical density: the more metal present, the darker the print. Platinum has a molar mass about twice that of palladium, therefore it takes about twice platinum by weight to give an image of the same optical density as palladium.

Papers and Printing

The tools, chemicals, and papers available to practitioners of the platinum printing process have changed over the past century,[10] and many types of platinum and palladium prints were produced. The closure of the Platinotype Company in 1937 marked the end of commercially available platinum papers for many decades. Printers wishing to produce prints today have to hand-sensitize their own papers.

Transitions

Paul L. Anderson (1880–1956), instructor at the Clarence H. White School of Photography and frequent proponent of Pictorialism, was a strong advocate for the platinum printing process, even after commercial platinum papers were no longer available. He frequently wrote about both platinum and palladium printing, comparing them with silver processing.[11] In his discussion of pictorial photography Anderson gave a detailed analysis of different printing methods, including their advantages and challenges.[12] He described both the use of commercial platinum papers

and the decisions faced when hand-sensitizing, such as the choice of paper and appropriate negatives. His instructions for preparing sensitizing solutions are shown in figure 10. They can be summarized as follows: Prepare two solutions of ferric oxalate sensitizer, one containing potassium chlorate. Mix these solutions in a drop-wise manner with the platinum (or palladium) salt solution to control the final contrast.[13] A greater proportion of potassium chlorate–containing sensitizer yields a print with more contrast, although this effect is greatly reduced for palladium papers. Anderson's recipes were often repeated in his and others' writings. They were rediscovered by Irving Penn in the 1960s and used by many well into the platinum revival.[14] Many printers continue to rely on Anderson's methods to mix their sensitizers.[15]

Despite the lack of commercial papers, chemical suppliers still marketed the precious metal salts specifically to the photography community (fig. 11). For example, Baker & Company sold palladium salts and related chemicals such as ferric oxalate (see fig. 11a). Karl Schumpelt at Baker took out a patent on the process, though it does not vary from Anderson's method,[16] and Anderson referred to Baker & Company as a source for materials in his later articles.[17] Paragon Testing Laboratories produced sensitized palladium printing paper (see fig. 11b) and acquired Baker & Company in 1940, continuing to distribute both products.[18] It is unclear whether many platinum printers used these materials. For instance, in 1941 Paul Strand

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Figure 12. Platinum print exhibiting a noticeable sensitizer stain, prepared at the National Gallery of Art. The paper was sensitized partway up the paper, leaving a border of unsensitized paper at the top. The print was masked on the right side and fully exposed on the left. After processing, a faint difference between the sensitized and unsensitized areas can be observed. After accelerated aging, these regions are more pronounced.
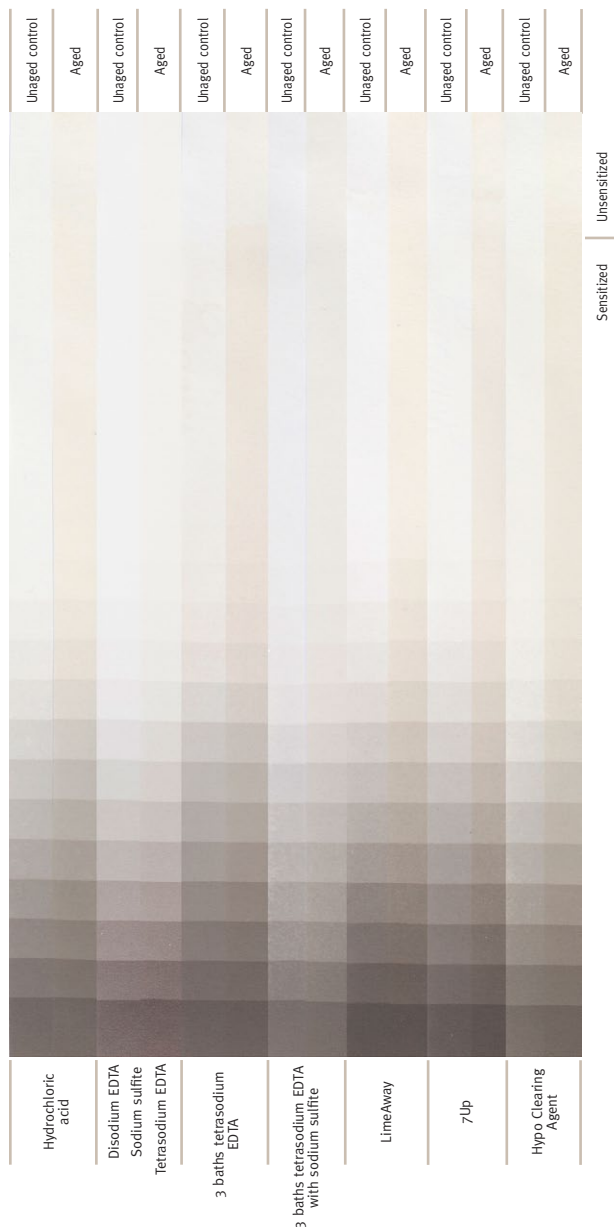
wrote that he was unaware of the production of the palladium paper.[19] Paragon was acquired by the Matheson Company in 1948.[20] No commercial platinum papers were sold until the short-lived Palladio Company was launched in the late 1980s.[21]

Modern Platinum and Palladium Printing

Platinum and palladium printing continues today. For the practitioner, many of the decisions faced when producing prints remain the same as a century ago.[22] While commercial platinum papers are no longer made, there are a greater number of options for making them using various combinations of metal salts and clearing agents. Current platinum and palladium printers may employ a range of platinum and palladium salts, such as lithium, sodium, potassium, cesium, and ammonium salts. Likewise, ferric oxalate may be substituted by ammonium ferric oxalate, sodium ferric oxalate, or lithium ferric oxalate. Each of these chemical modifications can impact the method in which the print is made and cleared.

The modern ammonium process employs ammonium ferric oxalate, first used for the print-out platinotype process by Giuseppe Pizzighelli in 1887.[23] This salt is very soluble, as is its photoproduct;[24] consequently, it will function as a print-out process if enough water is present in the paper to allow ion transport. The moisture content of the paper immediately prior to exposure determines the image tone: low water content leads to brown tones, whereas high water content leads to neutral tones. Under dry printing conditions, exposure to water vapor (such as over a bath at about 40°C) completes the development of the image. Adjusting the moisture in the paper is most easily performed by equilibrating it over saturated salt solutions or silica gel, after sensitization and before exposure. While mixing platinum and palladium salts is a common modern practice, it was recommended as early as 1895 by Baron Arthur von Hübl in *Der Platindruck*.[25] The importance of humidity was also noted by Alfred Stieglitz in 1891, who observed that dry papers yielded warmer tones when using Pizzighelli's "direct printing" paper.[26]

Figure 13. Platinum and palladium print step-tablets prepared at the National Gallery of Art on Crane & Company's 100% cotton paper (c. 1980s) by the ammonium process and cleared by several conditions, including traditional practice (1:200 HCl), common modern practice (baths of acidic and/or alkaline EDTA with or without a reducing bath such as sodium sulfite), and unusual practices (LimeAway, 7UP, or Hypo Clearing Agent). After aging, it is apparent that many clearing methods are not adequate. The 3-step method (disodium EDTA, followed by sodium sulfite, followed by tetrasodium EDTA) gives the cleanest appearing print after aging.

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Recent test prints sensitized using Pizzighelli's formula and equilibrated to varying levels of relative humidity confirmed these observations.[27] Additional investigations into the influence of humidity on modern platinum-palladium prints were also performed.[28]

As with the historic platinum methods, modern tests confirm that the chemicals used impact the final print appearance. Just as the different platinum and palladium salts used to sensitize papers have been adapted for use with new chemistries, so has the use of improved clearing agents. Hydrochloric acid may be used as a clearing agent, but at the higher concentrations typically used for platinum prints it can etch the small palladium particles. More dilute solutions, on the other hand, limit hydrochloric acid's ability to remove residual iron salts from the prints, and the iron salts will, ultimately, cause stains to form. Alternatives, such as sodium citrate–citric acid clear, advocated by the Platinotype Company for its Palladiotype process, are often not very effective, especially if clearing times are as short as those for platinum prints cleared with hydrochloric acid. The advent of modern chelators, such as ethylenediaminetetraacetic acid (EDTA), allows for more thorough removal of iron salts from papers. Like most chelators, the pH of the EDTA bath affects the degree of iron removal. Specifically, lower pH solutions allow for greater removal of ferric, $Fe(III)$, ions, while alkaline conditions remove more of the ferrous, $Fe(II)$, compounds. Such solutions are typically prepared from the sodium salts of EDTA. For example a 5% (w/v) solution of disodium EDTA yields a bath with pH 5, while a 5% (w/v) solution of tetrasodium EDTA has pH 11. Chelators, including EDTA, have also been explored for their applications in the removal of iron from stained historic prints.[29]

Print Processing and Longevity

Just as there are numerous ways to tailor a printing process to achieve a desired aesthetic, there are many ways to produce chemically dissimilar prints that look similar. The processing of a print includes many steps, the most exhilarating of which is watching the image's final speedy development. However, this excitement is followed by the tedium of removing the residual chemicals from the paper, a step that typically involves several baths of clearing solution followed by washing in water. Proper processing is critical to the final print's longevity because improper clearing of the print may not be readily apparent yet residual iron compounds from the sensitizer may remain. In fact, the effects of residual iron may not be noticeable for years or decades.[30] To better explore staining in prints, project collaborators prepared a large set of poorly processed prints by various means, employing a range of likely darkroom shortcuts.

Sensitizer Stain

Different types of staining in prints can occur. The stains that form over time due to insufficient removal of residual chemistry can become apparent as a "sensitizer stain," which refers to the yellowing in the highlights of a print that is not present in an area of unsensitized paper (fig. 12). In the sample prints, or "simulacra," prepared for this investigation, these areas are easy to compare. Many prints, however, lack unsensitized regions, having either been trimmed or been printed on paper sensitized to the edge. The presence of a black border may also make comparison challenging.

Abbreviated clearing and washing steps are the most likely causes of stain formation. Shortening the clearing time for prints was found to increase staining in prints, while shortening the washing time was not nearly as deleterious to the final print so long as the print was thoroughly cleared. A long washing time will not save an inadequately cleared print. XRF analysis of poorly processed platinum and palladium prints showed that abbreviated clearing times directly correlated with an increase in the residual iron within the paper, and this increase in iron was linked to an increase in stain formation after accelerated aging. In fact, prints that were processed with only ferric oxalate (no platinum or palladium in the sensitizer) and then subjected to an abbreviated clear also showed the formation of a sensitizer stain.

The Importance of Clearing

A number of clearing options were explored to determine the consequences of improper processing. These methods were tested on traditional platinum and palladium prints (potassium and sodium salts, respectively, with ferric oxalate) and the ammonium process (50:50 platinum:palladium combined with ammonium ferric oxalate). A portion of each print was subjected to accelerated aging. XRF analysis and colorimetry measurements were performed on the prints to determine the residual iron and color change. These studies demonstrated that the use of an acidic bath is crucial in the removal of the iron salts from the paper. Dilute baths, such as the 1:200 HCl solution typically used for palladium prints and the 1:120 dilution used for mercury-developed prints, remove less iron than the 1:60 bath, which is the recommended concentration for platinum prints. An acidic bath was especially important for prints prepared with ammonium ferric oxalate (fig. 13). The use of alkaline baths only, such

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Crane & Company's 100% cotton, c. 1980

Rives Bristol, c. 1970–80

Unaged control	Aged	Unaged control	Aged	Unaged control	Aged	Unaged control	Aged
Long clear		Short clear		Long clear		Short clear	
Disodium EDTA, sodium sulfite, tetrasodium EDTA				Tetrasodium EDTA only			

Figure 14. Platinum and palladium print step-tablets prepared by Pradip Malde using the ammonium process on two different papers. These were cleared using several conditions, including abbreviated processes. Portions of the prints were then subjected to accelerated aging. Although these two high-quality papers initially appeared visually similar and produced very similar prints, the differences in paper composition led to very different appearances post-aging. To inhibit the formation of stains regardless of paper type, the use of the 3-step clear that starts with an acidic bath and ends with an alkaline bath is recommended.
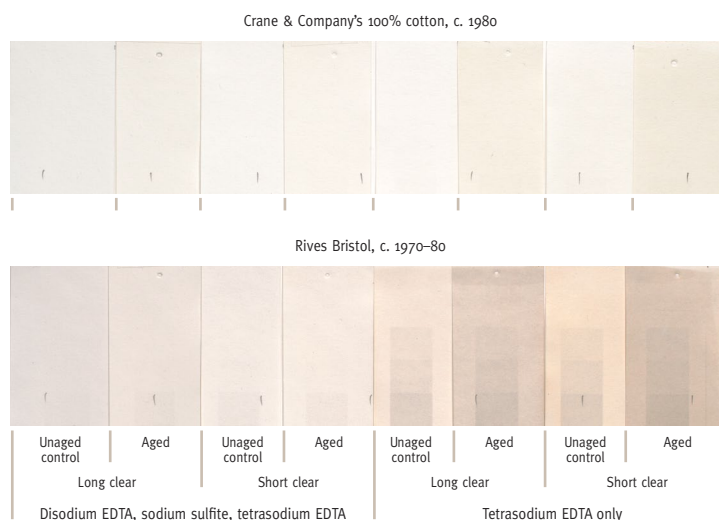
as tetrasodium EDTA (with or without the addition of a sodium sulfite reducing agent), resulted in a high iron reserve and led to a stained print after aging. However, an initial acid bath in a solution such as disodium EDTA gave superior results for all processes. The best results were obtained with a 3-step bath consisting of (1) disodium EDTA (5% w/v, pH 5), (2) sodium sulfite (2.5%), and (3) tetrasodium EDTA (5% w/v, pH 11). This 3-step bath is therefore highly recommended regardless of the paper support or sensitizer employed, as it consistently and efficiently reduced the residual iron.[31] Again, the paper base can significantly alter the efficacy of a given clearing agent. For instance, a comparison of two commonly used clearing methods (the 3-step bath and single bath tetrasodium EDTA), for two different papers with and without shortcuts, shows that staining can more readily occur on one of these papers for the single bath clear (fig. 14). Manufacturers and suppliers may change their formulations, sources of components, and procedures from batch to batch. While invisible to the consumer, these changes can cause unpredictable aging characteristics.
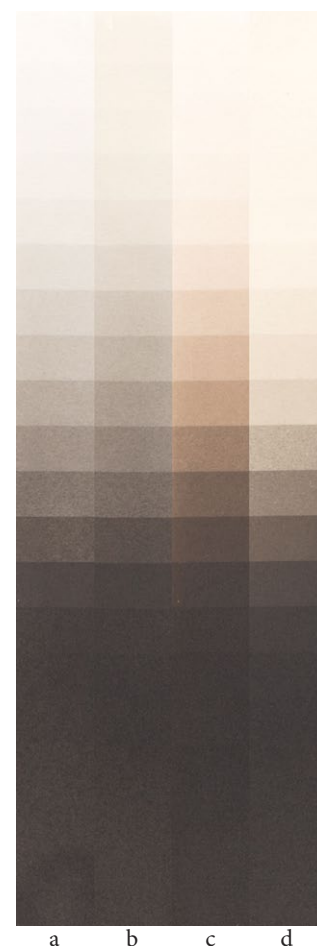
The Stability of Mercury-Processed Prints

A print's appearance may change with age. Papers may degrade and yellow and change the appearance of a print, and residual chemicals, such as iron, can react to form colored products. Toning metals may also interact with their environment over time and lead to change. Mercury was often added to platinum prints to give a more sepia tone and smooth the otherwise grainy appearance of the print. As mercury is not known to form an amalgam with platinum, some of this volatile element may depart the

print. As a case study, mercury-containing prints were examined in detail. Prints were prepared with mercury in the sensitizer and/or the developer, and the structure, metal content, and color changes that can occur when mercury is introduced as an additive were studied.

Indeed, accelerated-aging studies of simulacra confirmed that the quantity of mercury in platinum prints decreased, while the platinum concentration remained static, and that the image faded in proportion to the loss of mercury. However, some mercury remained in all cases. Prints that were

Figure 15. Platinum print step-tablets developed without and with mercury (1:2 Hg:developer), prepared at the National Gallery of Art. The platinum control exhibits little change before (a) and after accelerated aging (b). Prior to aging (c), the mercury-toned print has a warmer tone with a smoother appearance. After aging (d), the tone has become more neutral and the grain of the image more closely resembles the platinum control.

a b c d

Matthew L. Clarke, "Characterization, Degradation, and Analysis of Platinum and Palladium Prints," 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), 102–115.
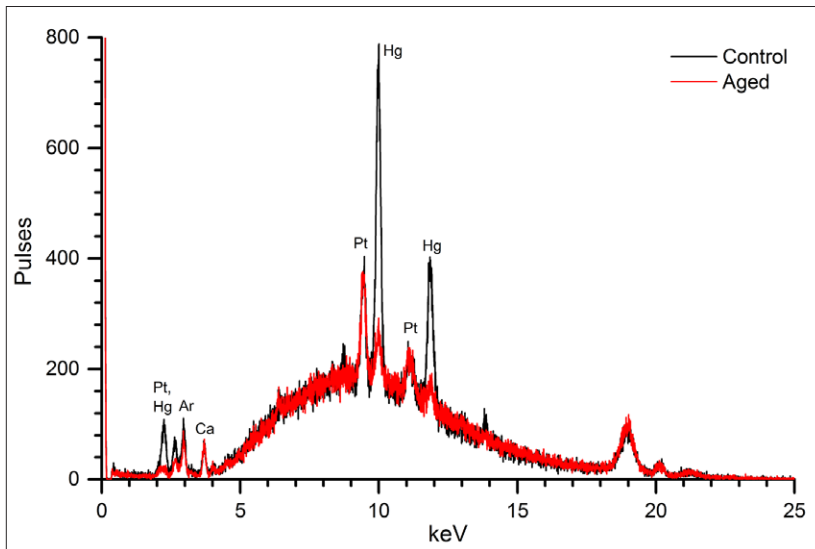
Figure 16. XRF spectra of a platinum print processed with a large amount of mercury in the developer. The large excess of mercury is not stable and sublimates during accelerated aging, while the amount of platinum remains the same.
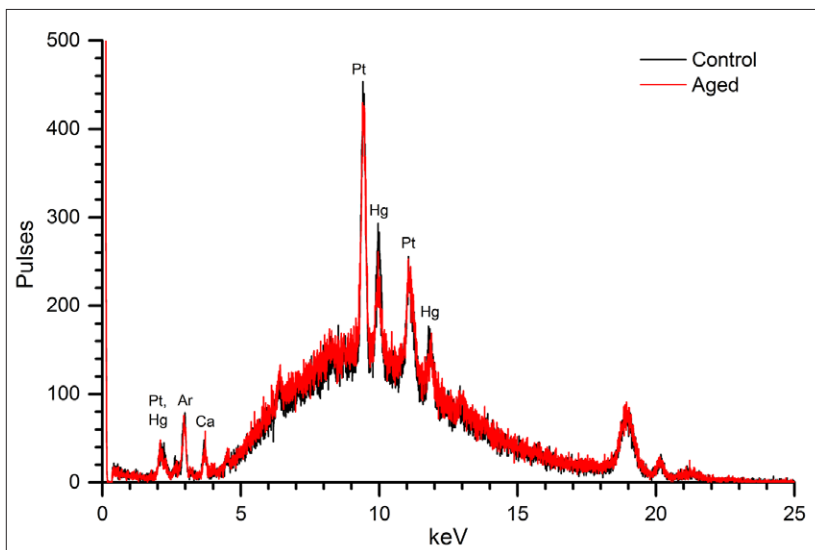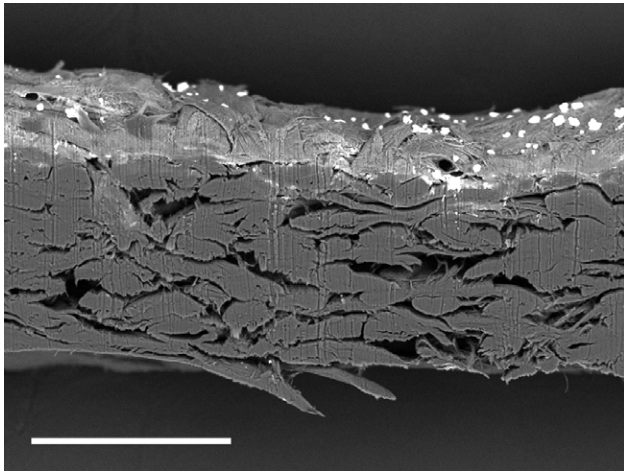

Figure 17. XRF spectra of a platinum print processed with mercury added to the platinum sensitizer. Some mercury is lost during accelerated aging; however, a larger proportion remains relative to the mercury-developed prints. The amount of platinum does not change after aging.

processed to produce a rich sepia image using a mercury-rich developer, and that initially retained high concentrations of mercury, suffered a distinct loss of the sepia color and an increase in image graininess after accelerated aging, resulting in appearance similar to untoned platinum prints (fig. 15). XRF analysis confirmed the loss of a large amount of mercury (fig. 16). Contrarily, when the initial amount of mercury was smaller, such as in the case of the prepared mercury-sensitized prints, the visual change upon aging was minimal and XRF confirmed only a slight loss of mercury (fig. 17). More detailed work is needed to understand the interaction of platinum and mercury at the molecular level and to determine whether any amount of mercury can remain stably incorporated in a platinum print.[32]

Regardless of its ability to form an amalgam, platinum and mercury are known to interact. Small amounts of mercury have been found to be stable in platinum metal. Indeed, the poisoning of platinum catalysts by mercury has long been a topic of research.[33] Studies indicate several adsorption modes of mercury on the platinum surface. Adsorption isotherms showed that the first mercury desorption occurred at 100ºC, with some mercury requiring much higher temperatures.[34] This finding suggests that under accelerated aging conditions at 70ºC, the mercury that is adsorbed to the platinum crystal surface will

Matthew L. Clarke, "Characterization, Degradation, and Analysis of Platinum and Palladium Prints," 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), 102–115.

18a

18b

Figure 18. BS-SEM image of a mercury-developed platinum print. The very bright spots in the unaged sample (18a) exhibit high concentrations of mercury and chlorine by EDS. Mercury and platinum are both found in the upper surface of the print.
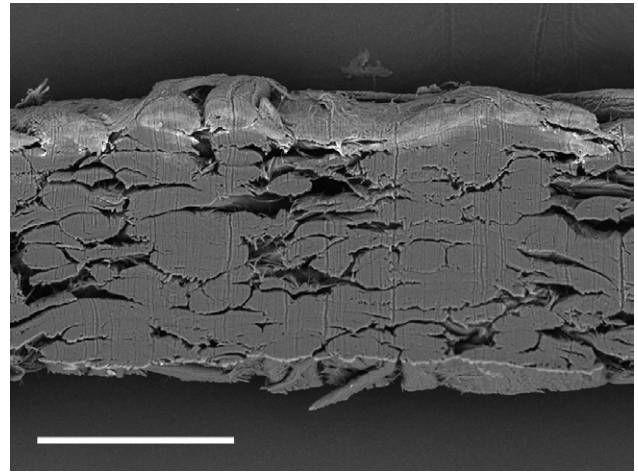
After accelerated aging (18b), the amount of mercury is significantly reduced. Scale bars = 100 μm.
  18a. Before accelerated aging.
  18b. After accelerated aging.

remain. Excess mercury used in the printing process will sublimate (fig. 18). The amount of stable mercury in the print may vary based on the initial printing conditions, and it can affect the particle size, surface area, and therefore reactivity of the platinum surface to mercury.

The loss of mercury from the print is not influenced by exposure to light. Microfadeometry analysis[35] was performed on both simulacra prints (before and after accelerated aging) as well as historic platinum prints processed with mercury. All prints were considered to be fairly lightfast. Only small changes due to bleaching of the paper degradation products were observed, such as a small loss of yellow from the paper.

During the accelerated aging of platinum simulacra containing mercury, one "plain" platinum print was included as a control. XRF analysis showed that this print acquired mercury (from the vapor present from the other prints) and that the mercury signal correlated with the platinum density (i.e., the mercury is bound to the platinum, not the paper support). Additionally, plain platinum prints that have been stored in close contact with mercury-developed platinum prints showed a trace signal of mercury after one year of storage. The long-term stability of mercury in these "contaminated" platinum prints has not been explored. However, such a phenomenon complicates the identification of mercury-processed platinum prints, particularly for prints where mercury is present in trace amounts. Placing mercury- and non-mercury-containing prints in individual enclosures, such as polyester sleeves, is recommended to minimize such crossover.

While platinum is not known to form an amalgam with mercury, palladium does, and a palladium mercury alloy can be found as the naturally occurring mineral potarite.[36] Historically, the toning of palladium prints with mercury was rarely performed, as it results in a minimal change in the aesthetic of the print. Adding mercury to palladium prints gives slightly cooler tones, an effect opposite the effect seen in platinum prints, and a less grainy appearance. Due to the stable interaction of palladium and mercury, palladium prints developed with mercury did not show a reduction in the mercury concentration after accelerated aging, nor was there a drastic color change. Additionally, palladium prints have the capability of picking up mercury from their local environment, such as in the case of storage of mercury-containing prints within the same enclosure.

Conclusions

Visual examination and analytical measurements of platinum and palladium prints can yield interesting and sometimes surprising details about the processes that created these evocative images. Regardless of whether the printer understands the chemical minutiae, the steps in the printing process are carefully chosen to achieve a given aesthetic. The wide range of materials and process variants used throughout the history of photography means that it may be impossible to determine the exact manner in which any given print was made. For example, prints may exhibit subtle differences that are not detectable by the common range of techniques typically employed by conservators and conservation scientists (fig. 19). While

Matthew L. Clarke, "Characterization, Degradation, and Analysis of Platinum and Palladium Prints," 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), 102–115.

instrumental methods are often available to distinguish platinum prints from palladium, or determine if mercury was added during processing, questions remain that are challenging to answer but should be explored.

Acknowledgments

Appendix

Making Platinum and Palladium Prints

A large number of sample prints were prepared at the Photograph Conservation Department, National Gallery of Art, as well as by other contributors to the project. Hundreds of test prints were created, carefully controlling many of the variables present in the printing process. The basics of the printing, clearing, and accelerated aging procedures are detailed here. See also Caroline Minchew, "A Step-by-Step Guide to Platinum and Palladium Printing," in this volume.

Paper Support

Selecting a paper base was the first step in the process. For the bulk of the prints prepared, an alum rosin–sized 100% cotton paper was selected; it had no dyes, optical brightening agents, or an alkaline reserve such as calcium carbonate. This paper was obtained from several long-discarded boxes of National Gallery of Art letterhead, c. 1980, which did vary by batch. For any particular study, a single paper source was employed.

Sensitizers

The traditional platinum process was prepared by sensitizing the paper with ferric oxalate and potassium tetrachloroplatinate. For palladium printing, sodium chloropalladate replaces the platinum salt. A 21-step-

Figure 19. Rockwood Studio New York, [*unidentified portrait*], c. 1900. Platinum prints, both 12.6 × 8.8 cm. National Gallery of Art, Photograph Conservation Department Study Collection. Despite distinct differences in tonal appearance, XRF did not reveal a difference in the elemental composition of these prints.

113   Matthew L. Clarke, "Characterization, Degradation, and Analysis of Platinum and Palladium Prints," 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), 102–115.

tablet negative was used for the exposure by a UV facial-tanning solarium. Exposed prints were developed in potassium oxalate solution acidified with oxalic acid. The prints were subsequently washed and cleared. In the case of mercury-toned prints, saturated solutions of mercuric chloride were added to the potassium oxalate developer solution, varying the ratio of the two solutions.

Clearing and Washing
Inadequate removal of the remaining platinum (or palladium) and iron salts is a common concern for the long-term stability of these prints. Large variations in clearing and washing times were employed to determine their effects. For example, a thoroughly cleared print was treated to 3 baths of clearing solution (such as 1:60 HCl for a platinum print) for 10 minutes each. Short-cleared samples received only 2 minutes in each bath. The exact times of the baths varied depending on the particular test. Washing times varied from 2 minutes to 30 minutes, and varied from constantly running water to trays of water containing higher iron content.

Experiments showed that short clearing times led to more dramatic staining in prints than short washing times. In other words, a poorly cleared print stained regardless of washing times, whereas a poorly washed print that was properly cleared did not.

Aging Prints
Accelerated aging was performed in an Espec humidity chamber for 4 weeks at 70ºC and 75% RH. The samples were strung on polyester filament tied to a stainless steel scaffold. The aging conditions were chosen based on initial tests showing this range was suitable to show staining for poorly processed prints, while minimizing degradation of the paper base.

Notes

1. See Mike Ware, "The Technical History and Chemistry of Platinum and Palladium Printing," in this volume.

2. For more information on the platinum-silver processes, see Ware, "Technical History and Chemistry of Platinum and Palladium Printing"; Constance McCabe et al., "Satista Prints and Fading"; and Ronel Namde and Joan M. Walker, "Platinum Toning of Silver Prints," in this volume. Namde and Walker have shown the challenges in distinguishing platinum-toned silver prints, Satista prints, and silver-intensified platinum prints.

3. Enyeart et al. 1983; McCabe and Glinsman 1995; Grieten and Casadio 2010; Stulik and Kaplan 2012.

4. Typical measurement settings: ArtTax XRF spectrometer, Rh tube with capillary optics, 45 kV, 550 µA, 120 s. Ideally, measurements are performed with the samples supported over an air backing to minimize the influence of extraneous materials, such as mount boards, and reduce the signal from inelastic scatter.

5. ATR-FTIR may be used to identify other components of the photograph, such as coatings. See McGlinchey and Maines 2005, 39–42.

6. Backscattered scanning electron microscopy was performed on cross sections prepared by microtome. The samples were coated with 15 nm of carbon and analyzed at 10 Pa with a 10 kV accelerating voltage.

7. Centeno et al. 2014; Clarke et al. 2014; Clarke et al. 2015.

8. See Matthew L. Clarke et al., "Platinum Prints on the Nano Scale," in this volume.

9. The metal density is calculated through XRF measurements calibrated to thin film standards prepared by Micromatter, Vancouver, Canada. The analysis is similar to that described by Stulik and Kaplan 2012, 104–6.

10. The early history of the process is well considered by Ware, "Technical History and Chemistry of Platinum and Palladium Printing," and Sarah S. Wagner, "Manufactured and *Faux Platinum* Papers, 1880s–1920s," in this volume.

11. Anderson 1940, 59–61.

12. Anderson 1917, 144–59.

13. Anderson 1923, 194–211.

14. See Tatiana Cole, "The Platinum Renaissance: Oral Histories of Platinum-Palladium Printers and Artists," and Vasilios Zatse and Constance McCabe, "Irving Penn's Platinum-Palladium Prints," in this volume.

15. Crawford 1979, 168–69.

16. Schumpelt 1941.

17. Anderson 1938; Anderson 1940, 61.

18. Paragon Testing Laboratories 1940; Rosenbaum 1941.

19. Strand 1941.

20. "Trade Notes" 1948.

21. See Cole, "Platinum Renaissance," in this volume.

22. For further details about the traditional and alternative printing processes, see Caroline Minchew, "A Step-by-Step Guide to Platinum and Palladium Printing," in this volume.

23. Pizzighelli 1888, 142–44.

24. Ware 1986.

25. Hübl 1895. Wall 1902 is a series of translated digests.

26. Stieglitz 1891, 249.

27. Prints prepared by Heather Brown using historic recipes during an internship at the Museum of Fine Arts, Houston, in collaboration with the National Gallery of Art.

28. See Clarke et al., "Platinum Prints at the Nano Scale," in this volume.

29. See Matthew L. Clarke and Dana Hemmenway, "Investigating Chelating Agents for the Treatment of Platinum Prints," in this volume.

30. See Constance McCabe et al., "Alfred Stieglitz's Palladium Prints: Treated by Steichen," in this volume.

31. Ware 1986.

32. See Erin L. Murphy, Christopher McGlinchey, and Adrienne Lundgren, "Reflective Sheen in Mercury-Processed Platinum Prints," in this volume.

33. Barbier 1985, 113–22; Dasari et al. 2013.

34. Affrossman et al. 1966.

35. See Christopher A. Maines, "Microfading to Predict Change," in this volume.

36. Spencer 1928.

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