Setting the Tone: Platinum Toning of Silver Photographs

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Abstract

From the earliest experiments in silver-based photography, methods have been investigated to increase the permanence and manipulate the tones of silver images. In 1856, Ernest de Caranza published the first example of a platinum-containing toning bath for salted paper prints. However, platinum toning did not gain popularity until the introduction of William Willis’s Platinotype process and the availability of more effective chemicals in the 1870s. Many amateur and professional photographers, including Alfred Stieglitz, published their own platinum toner recipes and tips in specialty journals as this exploratory phase continued, culminating in a widely cited treatise by Lyonel Clark first published in 1890. In subsequent decades, a great variety of toning bath compositions were proposed, which used different concentrations of platinum and other additives to achieve the desired tonal range.

Despite the wealth of period literature promoting the process, relatively few examples of platinum-toned silver prints have been identified in museum collections. The present research project aims to recreate historic recipes from published sources, focusing on the salted paper print. Subsequent analyses of simulacra will yield a better understanding of platinum’s use as a toning element in early photographs. A brief overview of documentary evidence relating to toning will be presented along with the preliminary results of the analytical investigation. Ultimately, analytical results will be tied to visual observations of prints, with the goal of contributing to process identification in the field and aiding in the elucidation of toning processes used by early photographers.

Introduction

From the earliest experiments in silver-based photography, methods have been investigated to increase the permanence and manipulate the tones of silver images. Gold toning of silver photographs was commonly employed early in the history of the medium for both daguerreotypes and print processes. Platinum toning was also mentioned in the period literature beginning in the 1850s. However, the practice of platinum toning of silver prints did not gain the same foothold in photography as gold toning, and it did not achieve any sort of popularity until the introduction of William Willis’s Platinotype process and the availability of more effective toning chemicals in the 1870s. Platinum toning was purported to impart colors distinct from gold toning, improve the permanence of those prints, and emulate the look of platinum prints at a lesser cost (Clark 1890). Despite this textual evidence, little mention has been made of the history of platinum toning beyond brief discussions of its use for toning salted paper, albumen, and matte collodion prints (Reilly 1980, 81-2; Pénichon 1999; Hofmann and Schatzl 2003).
Background

In 1856 French photographer Ernest de Caranza published the first example of a platinum-containing toning bath for salted paper prints (Assemblée 1856). The de Caranza recipe consisted of hydrochloric acid and platinum(IV) in the form of PtCl₄. Despite publishing the recipe, presenting his work at the Société française de photographie, and having it reproduced in both English and American photographic journals, the recipe was not widely adopted. The hydrochloric acid was thought to etch the image, thereby reducing the optical density of the prints significantly. Additionally, the commercially available platinum salt of the time, platinum(IV) chloride, also called bichloride of platinum or platinic chloride, has poor toning power because it is inefficiently reduced to metallic platinum.

From the late 1850s to the 1870s, various photographers experimented with platinum(IV) chloride for toning; however, it is unclear how successful these efforts were. Albums at the Bibliothèque nationale de France and the George Eastman Museum contain examples of prints made by various processes, toned with gold and/or platinum, and coated with different materials (Botelho 2001). Few other photographers wrote about platinum toning or inquired about it in photographic journals during this time, some suggesting the use of platinic sulfate or platinic nitrate instead of platinic chloride.

William Willis Jr. first patented the Platinotype process in the 1870s, and with it came the commercial availability of platinum(II) in the form of potassium chloroplatinite, now known as potassium tetrachloroplatinate (K₂PtCl₄). In 1887, Willis patented his cold-bath Platinotype, also known as the “platinum-in-the-bath” process (Willis 1887). In the platinum-in-the-bath method, the paper is sensitized with iron oxalate and trace amounts of mercuric chloride. After exposure to light through a negative, the partially printed-out image is developed using the platinum solution, fully replacing the iron image with platinum. The popularity of the Platinotype spurred a renewed interest in platinum as a toner for silver-based processes, and influential photographers such as Alfred Stieglitz quickly attempted to use Willis’s platinum-in-the-bath developer as a toning bath for silver prints (Stieglitz 1890).

In 1890, Lyonel Clark published his monograph *Platinum Toning*, which was widely cited and would be issued five subsequent times, again in 1890, then in 1892, 1895, 1897, and 1901. Clark’s innovation was to use an acidic bath with potassium tetrachloroplatinate. The interest in platinum toning increased rapidly during the 1890s, with many photographers publishing their own recipes or variations of ones that had previously been published and editors of photographic periodicals answering a growing number of questions about platinum toning. Interest persisted into the early twentieth century, coinciding with the height of platinum print popularity and the so-called “salted paper print revival.”

Toning recipes appear in photographic encyclopedias, manuals, and dictionaries from the 1890s through the 1930s and were not limited to the salted paper print process. The editors of *The Photographic News* stated that “[a]ny gelatino or collodio-chloride paper, whether matte or glossy, may be toned with platinum,” and a 1914 British encyclopedic journal gives recipes under headings for “Plain Papers,” “Gelatine P.O.P,” “Collodio-Chloride P.O.P,” and “Bromide and Gaslight Papers” (“Our Consulting Room” 1898; Brown 1914). Photographers made
reference to toning silver prints of many varieties, including salted paper, albumen, collodion, and gelatin, whether printed-out or developed-out.

Various commercial silver papers were specifically formulated for platinum toning, including Albumat, an albumen printing-out paper; Aura self-toning collodion printing-out paper; Aristo Platino collodion printing-out paper by American Aristotype Company; Sylvio Matt paper by Wellington & Ward; and Matt Self-Toning Paper by M. Willie & Bro.; and Aristo Platinum Solution and Tonplatinol, among others, were marketed as toners for silver prints (fig. 1). In addition to toning a variety of papers, photographers claimed different tones could be produced with a single bath by stopping the toning at an earlier stage. Moreover, a range of colors, from reddish brown to purple and black, could be achieved by using toning baths of different compositions. Despite photographers’ assertions regarding the ability to tone just about any paper, and the availability of commercial papers sold explicitly for platinum toning, Tennant states in the 1899 Photo-Miniature that in the United States, platinum toning was primarily used on matte-collodion print-out paper (Tennant 1899).

During World War I, the number of published references that mention platinum toning decreased, likely due to the restricted use of platinum outside of war-related efforts, and it never again reaches the same level as during the pre-war years. Recipes are found intermittently over subsequent decades, including in some contemporary manuals on alternative processes.

**Experimental Design**

With the abundance of historic references and recipes for platinum toning of silver prints, the authors focused on photographers’ claims about the imparted colors, improved permanence, and
emulation of platinum prints. More broadly, the authors could begin to evaluate how regularly this practice occurred and potentially identify more of these prints in collections.

A range of toning baths was selected from period literature (Table 1), seven containing potassium tetrachloroplatinate and two containing platinic chloride. The two nitric acid recipes published by Clark, one for black tones and one for brown, are reproduced across the literature. Nitric acid appeared most frequently, followed by phosphoric and citric acids, in the published recipes for toning baths recommended for salted paper prints. This variety of acids allowed for the investigation of the effects of organic as well as inorganic acids.

The authors also tested the original Willis “platinum-in-the-bath” solution and Stieglitz’s published version of it. The notable difference between the two is that Stieglitz’s recipe called for potassium phosphate (K₃PO₄), while Willis’s developer used dipotassium orthophosphate (K₂HPO₄) (Willis 1888; Stieglitz 1890). However, it is unclear if the change in bath composition was a deliberate choice by Stieglitz, an error in publishing, or confusion in nomenclature for the same chemical. These “platinum-in-the-bath” recipes had the highest concentrations of platinum of the baths tested, and were the only alkaline toning baths.

Two platinum(IV) baths were examined: the first published in 1856 by Ernest de Caranza, and a 1905 recipe that represents one of the few platinum(IV) baths published after the introduction of potassium tetrachloroplatinate. The 1905 Haddon recipe is accompanied by a note stating that, while the salt was not particularly suitable for toning, the recipe gave “pleasing” prints (Hasluck 1905, 249).

<table>
<thead>
<tr>
<th>Pt Salt</th>
<th>Bath Name (Reference)</th>
<th>[Pt⁴⁺] / mM</th>
<th>Other Bath Components</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₂PtCl₄</td>
<td>Nitric acid, conc. (Clark)</td>
<td>10.3</td>
<td>nitric acid</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Nitric acid, dilute (Clark)</td>
<td>2.7</td>
<td>nitric acid</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Phosphoric acid (Wall 1900)</td>
<td>4.8</td>
<td>phosphoric acid</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Citric acid, conc. (Wall 1902)</td>
<td>5.5</td>
<td>citric acid</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Citric acid, dilute (Jarman)</td>
<td>0.5</td>
<td>citric acid</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Willis “Pt-in-the-bath” developer (Willis)</td>
<td>27.0</td>
<td>dipotassium orthophosphate potassium oxalate</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>Stieglitz “Pt-in-the-bath” toner (Stieglitz)</td>
<td>15.1</td>
<td>potassium phosphate potassium oxalate</td>
<td>11</td>
</tr>
<tr>
<td>PtCl₄</td>
<td>de Caranza (de Caranza)</td>
<td>0.86</td>
<td>hydrochloric acid</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Haddon’s formula (Hasluck)</td>
<td>0.6</td>
<td>formic acid sodium formate</td>
<td>4</td>
</tr>
</tbody>
</table>

Salted paper prints were created following the processing procedure outlined by Lyonel Clark. Briefly, the paper was salted with an aqueous solution of 1.8% ammonium chloride in 2% arrowroot and sensitized with 14% silver nitrate containing 5.5% citric acid. The prepared sheets were exposed in an ultraviolet unit (Arista) under a 21-step Stouffer’s gray scale negative for 12
minutes. Prints were then washed in multiple changes of water and toned using one of the baths discussed above.

Full sheets (8"×10") were used for each toning test. After exposure, the prints were cut into five strips. For each sample sheet, a section was left untoned for reference. Each strip was toned for 15 seconds, 30 seconds, 1 minute, or 2 minutes, respectively (fig. 2). Specific toning times were not given in the literature, so these times were judged empirically.

Prints toned in acidic conditions went through a neutralizing bath (1% NaHCO₃) before being moved into the fixing bath (15% sodium thiosulfate), while prints toned in alkaline baths were placed directly into the sodium thiosulfate fix. All prints were fixed for 10 minutes, washed in running water, and then air dried. Of the toned samples, half of each was aged for 4 weeks at 70 °C and 75% relative humidity (Espec BTL-433). The prints were analyzed by X-ray fluorescence spectroscopy (XRF), microfade testing, colorimetry, and densitometry before and after aging.

Figure 2. Schematic of the full sheets used for each toning and aging test.

Results

Salted Paper Print

The data from the untoned salted paper print serve as a baseline and reference point for the other data collected. For the purposes of this analysis, D-min is step 1 and D-max is step 21. The darker the step, i.e. the greater the optical density, the more silver is detected in the XRF spectrum, evidenced by the intensity of the Lα peak at 2.98 keV.

The untoned salted paper print is purplish black in color and becomes a redder-brown after aging, as represented in the CIE L*a*b* plots (fig. 3). For the L* value, there is a minor shift in the midtones after aging, indicating slight lightening in this region. The print increases in the a* value, becoming redder in the later midtone range. Overall, there is a marked increase in the b* value, corresponding to the general yellowing of the sample.
K₂PtCl₄ Recipes

Clark’s Nitric Acid Recipes

Clark’s nitric acid recipe for “black” tones calls for the highest amount of platinum among the acidic recipes examined. After only 15 seconds in the toning bath, there is a noticeable color change and some bleaching when compared with the untoned salted paper print. The amount of silver decreases with each successive toning time interval, while the amount of platinum increases (fig. 4)

Figure 3. Colorimetric data for the untoned salted paper print, before and after aging. There is a lightening of the midtones (L*), increase in redness (a*), and increase in yellowness (b*).

Figure 4. XRF data for salted paper print toned with the concentrated nitric acid recipe showing the increase in platinum and decrease in silver intensity as a function of length of time a sample was toned.
The samples lighten after toning as represented by an increase in the $L^*$ value, likely representing a combination of acid action on the silver and platinum replacement of silver particles through galvanic replacement. After toning, the samples show decreases in the $a^*$ value and increases in the $b^*$ value, becoming less red and more yellow (fig. 5). Those trends are noticeable when examining the actual samples.

After toning, the optical density of the image decreases and continues to decrease the longer the samples are toned. Furthermore, a greater total amount of change (represented as $\Delta E$) is observed due to combined color and density shifts (fig. 6). After aging, the tones of the samples shift slightly in the $a^*$ and $b^*$ values, as shown in the data for the sample toned for 2 minutes (fig. 7). However, when compared to the aging behavior of the untoned salted paper print, the color shift is minimal.

Figure 5. Colorimetric data for the samples toned with the concentrated nitric acid recipe. For successive toning time intervals prints became lighter ($L^*$), less red ($a^*$), and more yellow ($b^*$).

Figure 6. Colorimetric and densitometric data for the samples toned with the concentrated nitric acid recipe. The densitometry (O.D.) shows the drop in optical density after toning. The colorimetry ($\Delta E$) shows the total change from the untoned salted paper print.
Clark’s dilute nitric acid recipe for “brown” tones has ¼ the platinum of the recipe for “black” tones and is about ten times less acidic. The trends seen with the “brown” tone bath are similar to those of the concentrated bath. XRF data reveal a decrease in the silver counts and a simultaneous increase in the platinum counts as toning progresses (fig. 8).

In aging, the degree of color change between the unaged and aged toned samples is much less than that between the unaged and aged salted paper print, indicating that the platinum content has a protective effect on the image (fig. 9).

**Dilute Citric Acid Recipe**

The same trends in the XRF, color, and aging data are repeated across the five acidic potassium tetrachloroplatinate recipes tested. Even the dilute citric acid recipe, which contains about 5% the platinum as Clark’s concentrated nitric acid bath, shows similar toning action, albeit to a reduced degree.
After the maximum toning time of 2 minutes, the platinum signal is significantly weaker in the XRF spectrum compared to samples toned in the more concentrated baths at this time-point (fig. 10). There is also a more gradual shift in color from the salted paper print through the 2-minute toning interval. In fact, the citric acid 2-minute toning interval is comparable in magnitude of color change to the 15-second toning with the concentrated nitric acid recipe (fig. 11). In practice, this type of variation and control over the toning process may have given photographers a means of achieving a desired aesthetic or result, such as nuanced color or tonal variation.

Willis and Stieglitz Recipes

The potassium tetrachloroplatinate recipes that stand apart are Willis’s “platinum-in-the-bath” developer and Stieglitz’s toning variation. For both recipes, very little platinum deposition is observed, and the silver peak intensity is virtually the same as the untoned salted paper print.

These recipes are also remarkable because there is a minor but noticeable increase in

Figure 9. Colorimetric data for the dilute nitric acid 2 minute toning interval, before and after aging. Similar to the concentrated nitric acid recipe, the toning has a protective effect on the print.

Figure 10. XRF data for salted paper print toned with the dilute citric acid recipe showing the increase in platinum and decrease in silver intensity as a function of length of time a sample was toned.

Figure 11. Total color change (ΔE) comparison for the citric acid 2-minute toning and the concentrated nitric acid 15-second toning interval.
optical density the longer the samples are toned, which is more pronounced in the Stieglitz variation than the Willis recipe (fig. 12). Clearly, a different platinum deposition mechanism for the alkaline baths as compared to the acidic baths is indicated. More detailed mechanistic investigations to resolve the difference in toning action will be the subject of a future publication.

Figure 12. Willis’s and Stieglitz’s toning recipes result in similar trends in metal deposition and optical density. There is a slight increase in optical density the longer samples were toned, although very little platinum is deposited.

The color shift appears to be tied to both pH and platinum concentration. However, within an acidic pH range of 1 to 3 with a platinum concentration between 2 and 10 mM, various baths are comparably efficient in toning action, regardless of acid. Interestingly, in 1912 the Lumière brothers and A. Seyewetz published a comparison of acids used in platinum toning (Lumière 1912). Prints produced on collodio-chloride and plain papers at various intervals showed little appreciable difference between baths made using sulfuric, nitric, phosphoric, citric, and lactic acids. This study agrees with the present results: within a certain platinum concentration, the identity of the acid has little effect on toning action.

Trends for K₂PtCl₄ Containing Recipes

As a whole, the recipes using potassium tetrachloroplatinate are efficient toners. When compared to the dramatic difference in color between the unaged and aged salted paper print, platinum toning improves permanence as many photographers claimed. For the acid-based recipes, there is only a minor loss in density during toning, despite many photographers advocating for overprinting to levels comparable to those for gold toning when preparing to tone. Additionally, there appears to be some validity to the claims made by practitioners that a range of tones could be achieved both by removing a print from a bath earlier and by using baths of different compositions and concentrations. It takes very little platinum to cause a color change, and in as little as 15 seconds, most of the toned samples display a discernible tonal shift from the untoned salted paper print of the same sheet.
PtCl₄ Recipes

The only recipes tested using platinum(IV) were the de Caranza recipe and Haddon’s formula. The Ernest de Caranza recipe calls for hydrochloric acid and platinum(IV) chloride. Only small amounts of platinum are deposited, but a large amount of silver is etched away, even in as little as 15 seconds of toning (fig. 13).

![XRF Spectra for De Caranza](image)

Figure 13. XRF data for de Caranza-toned samples showing the decrease in silver intensity as a function of length of toning and minor increase in platinum counts.

The samples lighten significantly after toning and become more neutral in hue. Although different in composition, Haddon’s formula performs similarly to the de Caranza recipe. Samples toned in either of the platinum(IV) recipes lose significant optical density and contain only small amounts of platinum. As might be expected with this overall lightening and decrease in optical density, there is a greater shift in ∆E from the salted paper prints than with the potassium tetrachloroplatinate recipes.

![Platinum and Silver Amounts](image)

Despite the loss in image density, the toning with Pt(IV) does impart protection against the effects of aging as seen in the colorimetry data (fig. 15). However in actual practice, the resulting photographic image may have been very low in both density and contrast and would have had to be overprinted very heavily to compensate for the dramatic bleaching effect of the bath.

![Optical density (O.D.) and total color change (∆E) of the de Caranza formula from the untoned salted paper print](image)

Figure 14. Optical density (O.D.) and total color change (∆E) of the de Caranza formula from the untoned salted paper print.
Conclusions

Some general conclusions can be drawn from this preliminary investigation. Very little platinum deposition is needed to impart a visual color change to the silver image, and a variety of tones can be obtained from the different published recipes. Platinum toning confers some degree of protection against the effects of aging, as toned samples shift less in color during artificial aging than do untoned salted paper prints. The most noticeable color change was consistently seen in midtones, where both changes in the paper base and image material impact the measured color.

Future Work

While this project has answered some questions about the use of platinum as a toning agent, it has also raised a number of others as avenues for future research, some of which are being actively investigated. Further investigation of where platinum toning fits in the larger practice of toning silver prints, especially as it relates to palladium, gold, and combined gold-and-platinum toning has begun to contextualize this practice in the larger field. Additionally, comparing platinum-toned salted paper prints with other platinum/silver processes (such as silver-platinum papers and silver-intensified platinum prints), in terms of image quality and through analysis, would potentially help explain the differences that may exist between these processes. The work presented here is a small fraction of the investigation that remains, and additional inquiries have yet to be fully explored.

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