Alfred Stieglitz’s Palladium Prints: Treated by Steichen

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Alfred Stieglitz (1864–1946) gained his impressive foundation in photographic science and chemistry as a student in Berlin under the distinguished German photographer Dr. Hermann Wilhelm Vogel (1834–1899). Stieglitz mastered many photographic processes and techniques, and he established his reputation by sharing his knowledge openly through his extensive writings.1 However, he never published his investigations into Palladiotype, the palladium photographic paper introduced by William Willis Jr’s (1841–1923) Platinotype Company in 1917,2 which he used to create some of his most acclaimed photographs. Stieglitz’s palladium prints exhibit a much greater creative range than those of many other leading photographers, including Edward Weston (1886–1958), Edward Steichen (1879–1973), and even Paul Strand (1890–1976).

Stieglitz understood the photographic chemistry as well as any of his contemporaries and demonstrated competence in and appreciation for making permanent photographs—ones that would not fade or change color. The vast majority of Stieglitz’s platinum and silver prints remain in excellent condition, but by the time of his death some of his palladium prints had developed disfiguring yellow-orange staining in the highlights that ranged from a slight mottling to an overall darkening (fig. 1).3 In 1949 his widow, the painter Georgia O’Keeffe (1887–1986), asked Steichen to perform a restorative chemical treatment for “certain prints of Stieglitz that look stained.”4 Steichen tackled the immense job of treating at least 232 palladium prints, improving their appearance enough to satisfy O’Keeffe’s demanding standards, yet he never disclosed his chemical treatment process.5

By 1989 Douglas Severson, the photograph conservator at the Art Institute of Chicago, observed the reappearance of the yellow staining in Stieglitz’s palladium prints.6 In 1995 Severson published a detailed account of a preliminary investigation of prints treated by Steichen, which provides essential background not addressed in this essay. Severson summarized the observations of scholars assembled at a 1993 colloquy at the National Gallery of Art on the topic of Steichen’s treatment of Stieglitz’s palladium prints, stating: “The vast majority of Stieglitz’s palladium photographs must have undergone at least two dramatic changes: (1) discoloration from their original state sufficient to require treatment, and (2) restoration to a ‘very much improved’ appearance after the treatment. But have these photographs continued to change over the past 40 years? If so, is it because of the treatments or in spite of them?”7

While Steichen’s treatment initially appeared to be successful, the reappearance of staining motivated the present long-term investigation to understand what caused the initial staining to occur, what chemical treatment Steichen used to clear them, and what caused the stains to regenerate.

Because neither photographer published his working methods relating to Palladiotypes—Stieglitz’s procedures for processing Palladiotype prints, or Steichen’s process for treating staining in Stieglitz’s prints—this investigation had to proceed largely by experiment, first trying to regenerate the stains seen in Stieglitz’s prints and then trying to re-create Steichen’s treatment to remove them. Fortunately, Stieglitz did describe some aspects of his palladium printing in personal letters, and these were helpful in trying to re-create his process in the laboratory.
Alfred Stieglitz's Palladiotypes

Palladium prints, like platinum prints, have a reputation for permanence, but the longevity of any photograph is dependent on many factors, not the least of which is the care exercised in its original processing. It seems unlikely that a photographer of the technical caliber of Alfred Stieglitz would ignore his own advice to "call a halt to our slipshod and sloppy technical manipulations and methods and revert to some measure of the old-time care and thoroughness." However, he boasted about how quickly he processed his Platinotypes. If he processed his Palladiotypes equally quickly, any chemical shortcuts may have contributed to the staining observed by O'Keeffe some twenty-five years later.

Stieglitz preferred the platinum process above all others, but when commercially manufactured platinum papers became increasingly difficult to obtain during World War I, he began to experiment with a variety of other photographic print processes. When Alfred Clements, Willis's business partner at Willis & Clements of Philadelphia, suggested that Stieglitz try the Platinotype Company's platinum-silver Satista paper, Stieglitz responded, "I am a pretty busy man and I have to steal the minutes for my photographic experiments. I am so at home with platinum, having used it since 1883, virtually to the exclusion of anything else, that I hate the idea of having to find a substitute." Stieglitz did try Satista along with a wide range of gelatin silver bromide and other papers, including the Platinotype Company's Palladiotype paper, which was sensitized with salts of iron and palladium, and first introduced in 1917 (fig. 2). Stieglitz continued to make prints in each variety of "Palladio" as it appeared on the market, including papers with both Japine and matte surfaces, with sepia and black image hues, and on white- and buff-colored paper.

Stieglitz wrote about his Palladiotype printing experiences to colleagues and friends, including Paul and Rebecca Strand, from New York City and from his family's summer home in Lake George, New York, where he made many of his Palladiotypes. These letters provide clues regarding his working methods and offer a glimpse into the trials and successes that Stieglitz encountered as he explored the "elasticity" of Palladio.

Stains in Stieglitz's Palladiotypes

Stieglitz made few prints of any given negative, and when he made more than one he often interpreted them differently (fig. 5). The prints may be light or dark, sepia or warm black, and the color of the paper base (soft white to creamy buff) influences the overall tone. These factors alone make it difficult to judge whether the current level of...
Figure 4. Alfred Stieglitz, Georgia O’Keeffe, possibly 1918. Palladium print, 19.2 × 23.4 cm. National Gallery of Art, Alfred Stieglitz Collection, 1980.70.21. This example of a black Palladiotype displays the appearance often associated with a platinum print.

Figure 5. Alfred Stieglitz, Charles Duncan, 1920. These two prints from the same negative were exposed for different lengths of time to achieve different interpretations.


5b. Palladium print, 23.8 × 19.5 cm. National Gallery of Art, Alfred Stieglitz Collection, 1949.3.428.
disfiguring staining in Stieglitz’s palladium prints is more or less than that observed by O’Keeffe in 1949, when she sought Steichen’s help in reducing the discoloration.

The potential for yellow staining is, in fact, difficult to predict when a print is newly made, and its presence in a print, either when new or decades later, may be difficult to discern. A yellow stain may be masked to some degree by the presence of a buff-colored paper base, especially in an image that has little or no highlights from which to judge. However, it is unlikely that prints with severely yellowed low-density image areas appeared this way when they were first made. Further, prints that were successfully treated for stain by Steichen and looked “newly made,” according to a key observer, should not, in any case, have the yellow highlights that disfigure them today.

The tone of a print may also be influenced by how well it was processed. If it was not properly cleared and washed during original processing, the residual sensitizer (the light-sensitive coating on the paper) can eventually form yellow-orange “sensitizer stains” visible in the highlights of a print. Stieglitz’s darker palladium prints provide little evidence of stain because they lack low-density image areas in which stains would be visible. However, the varying degrees of stain seen by Severson in 1989 and by observers today in the lighter portions of some prints point to Stieglitz’s lack of thoroughness in the original processing and to the limitations of Steichen’s subsequent chemical treatment. Evidence of the relative care taken in processing can be found in sensitized but unexposed areas of a print, such as the edges of prints that were masked by printing.
frames. The presence or absence of this sensitizer stain is a good indicator of how thoroughly the print was processed. A properly cleared and washed print should have clear, bright highlights that match the color of the paper stock. A poorly processed print may appear clean immediately following processing, but over time residual iron from the sensitizer will form a stain (figs. 6, 7).

The staining seen in palladium prints may also be related to the many possible variables in the materials used to make a print, including paper type and thickness, pH, sensitizing formula, clearing agent, and water quality, as well as processing methods, including clearing and washing times. These are the variables investigated in this study. Additional variables relating to storage, display, and treatment history also influence how a print will age.

Instructions for Processing Palladiotypes
Willis & Clements offered ready-prepared developer and clearing salts, but also provided the recipes for mixing these processing chemicals. The recipe for Palladiotype developer for warm black tones consisted of sodium citrate (20% w/v) acidified with citric acid (2% w/v). Palladiotypes were then cleared in the same components as the developer, but highly diluted. The instructions for clearing and washing Palladiotypes are described fairly succinctly, but specific details regarding the volumes of solutions to be used are lacking. Following the developing of the print, Willis & Clement’s instructions say that “Palladio Papers cannot be cleared quickly. Three baths of [the clearing solution] are necessary giving 10, 15, and 20 minutes in the first, second, and third baths respectively,” and that they must be washed “in running water for 10 or 15 minutes, or in several changes of 10 minutes each.” Further, a 1908 Willis & Clements product brochure specifically states that prints on Japine, the Platinotype Company’s proprietary Palladiotype according to the manufacturer’s instructions would be approximately 80 minutes per print:

- developer (1 bath, 3–5 minutes)
- clear (3 baths, 45 minutes total)
- wash (3 baths, 30 minutes total).

In addition, placing the negative in the printing frame and exposing the print to light could take from 5 to 50 minutes per print. So the total time it would take to complete the exposing and processing of a Palladiotype might be from 80 minutes to more than 2 hours per print. At the end of each processing session, careful air-drying of the prints would follow.

Stieglitz’s Printing Methods, Obstacles, and Shortcuts
Stieglitz boasted in a 1922 letter to Strand that, “I started proofing in Palladio. The first shot was at Bec’s hands. I got an astonishing result—exactly the thing I was after. Before the day was over I had used up 36 sheets & followed up to-day with another 24!! Some very good prints—fine color.” His claim of making so many prints in a single day suggests that he was not processing the prints thoroughly. The authors estimate that processing 24–36 prints should have taken 32–48 hours, but it is unlikely that Stieglitz ultimately determined all the prints made on these days to be a success.

Printing Methods
Stieglitz’s description of his printing and processing preparations in a 1923 letter to Rebecca Strand indicates that he was equipped for printing in mass production: “Day before yesterday I was finally ready to palladio. Negatives sorted—27 baths in a row—the sun out—day dry & clear—so the beginning. I had hardly gotten my three frames neatly set up when a tiny gray cloud came over the eastern hills.” It is unclear exactly how Stieglitz used the 27 baths, but a batch arrangement that would give the greatest number of thoroughly processed prints in the shortest amount of time might be as follows:

- 3 developer baths + 4 sets of 3 clearing baths
- 4 sets of 3 water baths = 27 total baths.

If the above scenario were used to properly process 4 prints at a time (not including setup or print exposure), the total time to develop, clear, and wash 36 prints would be 13 hours. It is difficult to imagine that 36 (or even 24) palladium prints could be both exposed and properly processed in a single day. Other tray arrangements, such as 1 developer bath, 3 sets of three clearing baths, and 3 sets of 5 washing baths, would have taken even longer. In his enthusiasm, did Stieglitz shorten the recommended processing times?

Obstacles: Printing Facilities and Water Quality
Stieglitz faced many obstacles in his pursuit of the perfect palladium print, including the lack of ideal darkroom facilities while working in New York City and the availability of pure water in Lake George to mix his chemicals and wash his prints. He complained about water quality several times:
As for the Palladio black buff I tried it out some weeks ago. . . . I have had some hard luck with good things. Grit in washing water—in spite of filter, etc., etc. 24

My photography of late is like a lame duck. . . . — developer gone awry through rust in the water in spite of improved filter. Palladio paper entirely misbehaving. 25

But there has been very much trouble with our water system — incompetency everywhere — — ghastly — my usual experience — — unbelievable. 26

**Shortcuts and Personal Motivations**

With his well-deserved reputation for both technical prowess and personal arrogance, Stieglitz may have simply chosen to ignore the Platinotype Company’s recommended processing protocols. In 1919 he wrote to Strand, “The palladio is here but I’ve had no weather for printing. . . . The directions are rather ambiguous in some respects.” 27 Two years later he wrote to Herbert J. Seligmann: “Using palladium. . . . I do nothing according to instructions. If I follow them I might as well throw the cans of paper into our blazing fires.” 28

The dearth of detailed written records of Stieglitz’s working methods for processing palladium prints makes it difficult to determine how to approach a technical investigation into the deterioration of his photographs. However, the few existing descriptions of his practices found in his letters clearly suggest that he did not fully follow the Platinotype Company’s instructions and was also hampered by the materials and facilities in which he did his processing. While the initial staining may have evolved from the original processing, how, and in what way, did Steichen’s treatment contribute to it?

**Edward Steichen’s Treatment**

Edward Steichen figured prominently in Stieglitz’s world. Together they founded the Little Galleries of the Photo-Secession at 291 Fifth Avenue in 1905, where the first exhibition of Steichen’s photographs was held in 1906. Philosophical differences caused them to part ways for more than two decades, but they managed to reconcile not long before Stieglitz’s death in 1946 (fig. 8).

**Recollections of Doris Bry**

Following Stieglitz’s death, O’Keeffe hired Doris Bry (1921–2014) (fig. 9), a recent graduate of Wellesley College, to assist with the sorting of Stieglitz’s estate’s collection of photographs, paintings, sculptures, and papers, in preparation for their distribution to nonprofit institutions. Bry worked as O’Keeffe’s trusted personal assistant for the next thirty years and played an instrumental role in the treatment project. Bry described the prints to the conservator Severson as being “very, very yellow and [they] gave you a feeling of disturbance.” 29

In 2001, Bry met with author Constance McCabe and colleagues at the Metropolitan Museum of Art, and she...
described additional details about Steichen's treatment of Stieglitz's prints. She explained that O'Keeffe had considered asking Paul Strand to help with the stained prints, but Stieglitz and Strand's relationship was strained in the mid-1930s. Among those O'Keeffe consulted regarding Stieglitz's estate was Edward Steichen, whose advice she sought on the preservation of the photographs. In spite of his busy schedule as the newly appointed director of the Museum of Modern Art's department of photography, Steichen agreed to treat Stieglitz's palladium prints to improve their appearance and longevity. Bry said that he probably did so because he felt he owed it to Stieglitz for help in his early days. Before learning that Steichen was prepared to perform the restorative treatment, however, O'Keeffe and Bry had destroyed some of the most severely discolored prints.30

Once arrangements were made for Steichen to treat the palladium prints, Bry worked closely with O'Keeffe to make the work as easy as possible for Steichen. O'Keeffe developed a system for maintaining the proper registration of the prints on the mounts and within the mats. Bry stated that she used a "good size" needle (big enough to handle and go through to the board) to put holes in the prints at the very corner of each window mat—at an angle—through to the backing board. Bry recalled that O'Keeffe said, "You wouldn't be able to see them, but they would be there" (see fig. 6a). Bry later also used pencil marks to maintain registration, finding them more satisfactory and easier to use than pinholes. Bry said the prints came off the mounts fairly easily and that she cleaned off residual adhesive by sanding or with moisture and light scraping. After Bry removed the prints from the mounts, she delivered them to Steichen in 8 ×10 inch boxes for treatment. She said she believed that Steichen performed the treatments himself and did not entrust an assistant with the work.31 According to Bry, the prints "came back looking clear and fresh ... newly made again" (fig. 10).32

Many of Stieglitz's prints were originally coated with beeswax and retouched to disguise flaws such as dust spots. These surface treatments further complicated Steichen's work. Bry said that coatings were removed by Steichen before his treatment, but not replaced afterward, and that O'Keeffe, who had retouched Stieglitz's prints for him during his lifetime, retouched the prints after Steichen's treatment.33

After the prints were treated and remounted, O'Keeffe or Bry annotated the mounts with the inscription, "Treated by Steichen," usually accompanied by the dates, which ranged from 1949 to 1951 (fig. 11). With the exception of a
few prints, such as some that had been acquired by museums during Stieglitz’s lifetime, the palladium prints were treated regardless of the degree of staining. According to Bry, Steichen was very secretive and would never respond when asked about his treatment, and he never revealed the exact nature of the treatment.

Recollections of Joel Snyder
An important clue regarding Steichen’s treatment was discovered when the photographer and photographic historian Joel Snyder revealed that he had contacted Edward Steichen in the late 1960s and asked him about his treatment of Stieglitz’s palladium prints. Snyder recounted that Steichen recalled using a “strong solution of sodium acetate” to reduce the stains and refraining from using hydrochloric acid because it would bleach the low-density image if fixed too long, diminishing detail. Steichen believed that sodium acetate did not “etch” or bleach the image, and that it did not change the hue of the image.

This new information led the National Gallery of Art investigators to test the efficacy of sodium acetate and other clearing agents that may have been available to Steichen in 1949–51 for reducing the appearance of staining in palladium prints. If any agents appeared to effectively reduce the staining without compromising the image, additional tests would follow to determine whether the improvement was permanent.

Table 1 | Preparation and Processing of First Set of Simulacra (City Tap Water)

<table>
<thead>
<tr>
<th>Developer</th>
<th>Proper Processing</th>
<th>Poor Processing</th>
<th>Proper Processing</th>
<th>Poor Processing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citrate Clear: Sodium Citrate (2.5% w/v) and Citric Acid (1% w/v)</td>
<td>5 min.</td>
<td>5 min.</td>
<td>5 min.</td>
<td>5 min.</td>
</tr>
<tr>
<td>Clear bath 1</td>
<td>10 min.</td>
<td>5 min.</td>
<td>10 min.</td>
<td>2 min.</td>
</tr>
<tr>
<td>Clear bath 2</td>
<td>15 min.</td>
<td>5 min.</td>
<td>10 min.</td>
<td>2 min.</td>
</tr>
<tr>
<td>Clear bath 3</td>
<td>20 min.</td>
<td>none</td>
<td>10 min.</td>
<td>2 min.</td>
</tr>
<tr>
<td>Wash</td>
<td>10 min. running tap water</td>
<td>1 min. running tap water</td>
<td>10 min. running tap water</td>
<td>1 min. running tap water</td>
</tr>
</tbody>
</table>

Three milliliters of sensitizer were applied in a line across each 19.5 × 20 cm area using a syringe, then distributed across the sheet using a glass rod. After drying, the sensitized paper was exposed by contact with a Stouffer Industries 21-step negative (TLF2115). The 8 × 10.5 in. simulacra were cut into strips. Each strip was developed for 5 minutes and then cleared and washed for varying times. Based on preliminary tests to generate moderate sensitizer stains upon aging, one set of strips was cleared in sodium citrate (2.5% w/v) and citric acid (1% w/v); one set was cleared in 1:200 hydrochloric acid; and both sets were washed in running city tap water according to recommended procedures. The remaining strips were cleared and washed for successively shorter times and in fewer baths, with the poorest processing occurring in a single 1 minute clear with a 1 minute wash. Filtered city water was used for all developer and clearing solutions (500 ml per 8 ×10.5 in. sheet), and running tap water was used for the wash. The samples were air-dried face up on Ahlstrom filter-paper-grade blotter paper.

Experiments to Generate Stains in Palladium Prints
The authors endeavored to reverse-engineer the stains seen in Stieglitz’s palladium prints. To do so, they had to select among an enormous number of possible variables to establish a repeatable set of materials and processes that might approximate the conditions that led to the stains. They also attempted to reproduce realistic shortcuts to which a photographer might resort if working in less-than-ideal conditions. The test prints, or simulacra, were then aged and analyzed by various methods to elucidate how different poor-processing procedures would affect them. The goal of the processing experiments was to produce prints that at first appeared “clear and fresh” but would display distinct stains upon aging. The defects in the test prints could not be conspicuous immediately after making them, as Stieglitz would have rejected any such prints.

The material and chemical characteristics of the simulacra, including paper support, palladium sensitizer, and processing conditions were selected to match Stieglitz’s palladium prints in the National Gallery of Art as closely as possible. However, Stieglitz did not personally sensitize his palladium papers. Rather, he purchased the Platinotype Company’s ready-sensitized Palladiotype papers for his prints, and the composition of that sensitizer is not known. Willis never patented his Palladiotype process; no written details about the fabrication of these papers have been discovered; and no examples of sensitized papers or prints made by the Platinotype Company were available for chemical analyses. The formula for the sensitizer, therefore, is a matter of speculation. The authors limited their test materials to one commercial paper and one palladium sensitizer formula, but varied the clearing materials, procedures, and conditions to clear and wash the prints.

Paper Support
To select a paper support that might approximate what Stieglitz used, the authors analyzed the paper composition of an untreated palladium print by Stieglitz and
several samples of sensitized but unprocessed Platinotype Company platinum papers. All samples contained similar alum-robin and starch components, which were assumed to be associated with the sizing. No proteins or gums were found.39

The closest match to the raw stock of the Platinotype Company papers was an off-white c. 1980s Crane & Company 100% cotton paper, sized with alum-robin and starch, unbuffered, and with no optical brighteners and apparently unbleached, and it was selected to prepare the palladium print simulacra.40 No specific product details regarding the Crane paper are known. It is thinner than the paper used for prints made by Stieglitz.

**Palladium Sensitizer**

The sensitizer selected for the simulacra was based on a composition comparable to Willis's Platinotype paper. It was made by mixing aqueous solutions of 25% w/v ferric oxalate hexahydrate and 2% w/v oxalic acid dihydrate with an equal volume of a 14.7% w/v sodium tetrachloropalladate(II) solution just prior to use (see tables 1, 2).41

Commercial Platinotype Company papers were invariably sensitized to the very edges of the sheets. The lack of any bare paper along a print’s edges makes it difficult to differentiate stains related to the sensitizer, where residual iron may be concentrated, from stains in the paper alone. To provide an area for comparison, sample prints were prepared leaving a border of unsensitized paper (fig. 12).

Three milliliters of sensitizer were applied in a line across each 19.5 × 20 cm area using a syringe, then distributed across the sheet using a glass rod. After drying, the sensitized paper was exposed by contact with a Stouffer Industries 21-step negative (TLF2115). The 8 ×10.5 in. simulacra were cut into strips. Each strip was developed for 5 minutes and then cleared and washed for varying times. Based on preliminary tests to generate moderate sensitizer stains upon aging, one set of strips was cleared in sodium citrate (2.5% w/v) and citric acid (1% w/v); one set was cleared in 1:200 hydrochloric acid. Unfiltered well water from Upper Marlboro, Maryland, was used to mix the developer and the clearing baths and to wash the prints in the second set of tests, and unfiltered well water from Lake George was used to mix the developer and the clearing baths and to wash the prints in the third set of tests. The volume of each clearing and washing bath was 500 ml per 8 × 10.5 in. sheet. The samples were air-dried face-up on Ahlstrom filter-paper-grade blotter paper.

**Table 2 | Preparation and Processing of Second (Maryland Well Water) and Third (Lake George Water) Sets of Simulacra**

<table>
<thead>
<tr>
<th>Developer</th>
<th>Citrate Clear: Sodium Citrate (2.5% w/v) and Citric Acid (1% w/v)</th>
<th>Hydrochloric Acid Clear (1:200 dilution)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proper Processing</td>
<td>5 min.</td>
<td>5 min.</td>
</tr>
<tr>
<td>Poor Processing</td>
<td>5 min.</td>
<td>5 min.</td>
</tr>
<tr>
<td>Proper Processing</td>
<td>5 min.</td>
<td>5 min.</td>
</tr>
<tr>
<td>Poor Processing</td>
<td>5 min.</td>
<td>5 min.</td>
</tr>
</tbody>
</table>

**Clear bath 1**

| Proper Processing  | 10 min. | 5 min. |
| Poor Processing    | 5 min.  | 10 min. |
| Proper Processing  | 10 min. | 2 min.  |
| Poor Processing    | 2 min.  |        |

**Clear bath 2**

| Proper Processing  | 15 min. | 5 min. |
| Poor Processing    | 5 min.  | 10 min. |
| Proper Processing  | 10 min. | 2 min.  |
| Poor Processing    | 2 min.  |        |

**Clear bath 3**

| Proper Processing  | 20 min. | none |
| Poor Processing    | 10 min. | 2 min. |

**Wash**

| Proper Processing  | 3 changes |
| Poor Processing    | 2 changes  |
| Proper Processing  | 3 changes  |
| Poor Processing    | 2 changes  |

| Proper Processing  | 10 min. each |
| Poor Processing    | 5 min. each  |
| Proper Processing  | 10 min. each |
| Poor Processing    | 5 min. each  |

Figure 12. Palladium print step-tablet simulacra made by the Photograph Conservation Department, National Gallery of Art. The first strip in the sequence was reserved as a control. The other three were then aged for 4 weeks at 70°C and 75% RH. The next strip in the sequence was reserved as an aged control. The two remaining strips were subjected to a sodium acetate reclearing treatment. The final strip in the sequence was re-aged for 4 weeks at 70°C and 75% RH. Note that the stain was reduced by the reclearing treatment, but upon re-aging the stain reappeared.
All simulacra were exposed with a standard step-tablet negative, with portions of the negative masked to allow both the plain paper borders and sensitized areas to be examined easily and to permit a comparison of the effectiveness of the clearing and washing procedure by close visual comparison of adjacent regions of a print.

Water
Water is the major component of the sensitizer, developer, clearing bath, and chemical treatment formulas, and the only component in the final washing steps. The purity of the water and the presence of contaminants have the potential to influence each photographic operation and the longevity of the resulting print. Therefore, only deionized water was used to prepare the sensitizer solutions, and Washington, D.C., tap water, filtered to remove chlorine and other significant contaminants, was used to mix the developer. The clearing solutions were prepared using both filtered city tap water (see table 1) and well water from two sources, (see table 2), and the water from these three different sources was also used to determine the influence of each on the final washing of prints, as described below.

Processing Chemicals and Methods
Simulacra were prepared to create prints that were both properly processed (thorough clearing and washing) and improperly processed (abbreviated clearing and/or washing steps). Both sets appeared to be free of the residual yellow-colored sensitizer immediately after processing, but upon accelerated aging for 4 weeks at 70°C and 75% RH, only the poorly processed prints produced visible stains. Each test was divided into four samples: before aging; after aging; after treatment; and after re-aging of treated samples (see fig. 12).

Sets of “control” simulacra were developed and cleared in sodium citrate and washed according to the Platinotype Company’s instructions, as described above: a total of 45 minutes in 3 citrate baths followed by a total of 30 minutes in 3 changes of water. Additional control sample prints were made using a 1:200 hydrochloric acid clearing bath, which was recommended for clearing by the influential Pictorialist photographer Paul L. Anderson in lieu of the sodium citrate/citric acid clearing solution.42

Additional sets of simulacra were subjected to several abbreviated clearing and washing protocols to induce staining upon aging. See tables 1 and 2 for details regarding the preparation of simulacra.

Preparation of First Set of Simulacra and Aging Conditions (City Tap Water)
To prepare for the initial accelerated aging tests, the sensitized paper was exposed and cut into strips. Each strip was then processed as shown in table 1 with varying clearing solution concentrations and wash times in running city tap water. After air-drying, the strips were compared. The abbreviated processing conditions that resulted in the step-tablets as having just the barest tinge of sensitizer stain in the nonimage area were judged as “acceptable in appearance” and reflect conditions that a photographer might have determined to be acceptable in appearance and did not yet reveal the flaws that would emerge upon aging (“poor processing” in table 1).

The simulacra were again cut into smaller strips. Half of each sample was reserved as a control and the other half was suspended by polyester filament from a stainless steel apparatus and exposed to accelerated aging conditions in an oven for 4 weeks at 70°C and 75% RH (see fig. 12). After aging, the sensitized area was visibly darker and more yellow than the adjacent unsensitized region of the paper in the poorly processed prints: moderate staining was visible in the areas that were sensitized but unexposed.

Multiple print samples were prepared and aged in this manner and then subjected to preliminary tests of treatments with several common re-clearing agents to determine their effectiveness in reducing stains. The results are discussed in detail below.

Preparation of Second Set of Simulacra and Aging Conditions (Maryland Well Water)
Based on the large number of trays Stieglitz used to process his prints at Lake George, it seems practical that he would have used exchanges of water in trays, rather than running water, to wash his prints. The authors’ concerns regarding both the influence of chlorine-treated water in New York City and the possible presence of iron in the water from Stieglitz’s source in Lake George, New York, led them to prepare a second set of poorly processed but acceptable-looking prints using unfiltered iron-containing well water from Upper Marlboro, Maryland, to better approximate the water Stieglitz might have used at Lake George. The simulacra made in this fashion were subjected to the conditions described above with the exceptions that the developer and the citrate and hydrochloric acid clearing baths were mixed using the well water and exchanges of well water in trays, rather than running city tap water, were used to wash the prints (table 2).
The second set of conditions for poorly processed but acceptable-looking prints did not produce deep staining. As previous experiments have shown, a poorly washed print will not stain significantly if it has been properly cleared, and a poorly cleared print will stain significantly regardless of wash times. It was decided to use standardized insufficient clearing protocols and a standard washing protocol, as they would maximize the time spent in the iron-rich well water, thus increasing chances of more extensive staining.

**Preparation of Third Set of Simulacra and Aging Conditions (Lake George Water)**

It is clear from Steiglitz’s correspondence that he struggled with high-iron water at Lake George. However, a water-quality report from 2009 from a well near Steiglitz’s Lake George estate revealed a substantially lower iron content than the content in the Maryland well water. A third set of simulacra was produced using unfiltered water from a well near Steiglitz’s house at Lake George for comparison; this water might more closely approximate the conditions Steiglitz would have encountered. The developer and both the citrate and hydrochloric acid clearing baths were mixed using the water from the Lake George well, and the prints were washed in the water from the Lake George well.

The simulacra were processed as shown in table 2. As with the first set of simulacra, the original Willis & Clements instructions for processing Palladiotype paper were used for the properly citrate-cleared and washed prints. The poorly processed citrate-cleared prints were cleared for a total of 10 minutes in 2 baths and washed for 10 minutes in 2 changes of water. Similarly, the hydrochloric acid–cleared sample prints were processed with both a thorough and an abbreviated clearing protocol.

Strips were removed from the simulacra and reserved as controls for comparison with the simulacra that were aged for 4 weeks at 70°C and 70% RH. Visible stains formed in the sensitized but unexposed areas of all sample prints; they were less intense than the stains seen in the Steiglitz prints treated by Steichen but were very similar in tone. As expected, the stains were worse in prints that were poorly cleared in both citrate and hydrochloric acid than in those that were properly cleared. That is, the prints with higher residual iron content produced worse stains.

**Experiments to Re-CREATE Steichen’s Treatments of Stained Palladium Prints**

A number of reclearing formulas were considered for testing in the present study. Several recipes were tested by author McCabe in 1993 as part of a preliminary study of the staining in Steiglitz’s palladium prints, including hydrochloric acid, which was used historically as a clearing agent for platinum and palladium printmaking. Hydrochloric acid was selected based on Beaumont Newhall’s uncertain recollection that Steichen used it to reclear the prints and on Anderson’s suggestion that it could be a substitute for sodium citrate, but at a far greater dilution than that used for platinum prints. Additionally, bleaching agents for reducing stains in platinum prints, including calcium hypochlorite and hydrochloric acid and calcium hypochlorite, were also tested as part of the 1993 study. Hydrochloric acid was found to be ineffective in reducing staining; the other agents were found to cause bleaching of the palladium image and/or paper support and were therefore not included in the present study.

When reclearing the stained prints, Steichen might have considered using the standard citrate–citric acid clear recommended by the Platinotype Company. Sodium acetate, which he indicated to be the clearing agent, could be used alone or acidified to improve its clearing properties. For this reason both 40% w/v sodium acetate (pH 10) and 40% w/v sodium acetate acidified with 20% w/v acetic acid (pH 5) were tested.

In an attempt to be more comprehensive than McCabe’s 1993 study, additional clearing agents to which Steichen might have had access were tested. It is a remote possibility that Steichen used ethylenediaminetetraacetic acid (EDTA) to reclear the Steiglitz prints, so the following clearing agents were tested:

- water as a control
- a nearly saturated solution (40% w/v) of sodium acetate solution (pH 10)
- a 40% w/v sodium acetate and 20% w/v acetic acid solution (pH 5)
- a conventional sodium citrate (2.5% w/v) / citric acid (1% w/v) clearing solution (pH 5)
- disodium ethylenediaminetetraacetic acid (Na₂EDTA), 5% (pH 5)
- tetra sodium ethylenediaminetetraacetic acid (Na₄EDTA), 5% w/v (pH 12).

Initial tests indicated little discernible reduction in staining after several hours, so all samples were treated for 24 hours with slow constant agitation. All the reclearing treatments visibly reduced the sensitizer stain to varying degrees, including the water bath and sodium acetate. The samples were measured by colorimetry to confirm the observations and analyzed by x-ray fluorescence (XRF) to determine if the treatments were effective in removing iron from the simulacra. The results
of the analyses of the samples at each stage of testing are presented in figures 13 and 14.

Experiments to Regenerate Stains in Treated Prints
After treating the simulacra with the above clearing agents, strips of the treated samples were retained for comparison after aging, and the remaining treated portions were re-aged at the conditions as described above (4 weeks at 70°C and 75% RH). Again, staining was induced. In general, the intensity of the stains that formed in the treated samples correlated well with how well the simulacra were cleared and how effective the reclearing treatments were in removing residual iron.

Discussion: Analyses of Collection Prints and Simulacra
The sets of re-aged simulacra were carefully examined and analyzed by XRF and colorimetry. Visual examination of the poorly processed, aged, recleared, and re-aged simulacra revealed that sodium acetate appeared to be only as effective as bathing with water alone in reducing the appearance of sensitizer stain. All of the other agents reduced the stains to greater degrees, including after re-aging.

It is quite likely that Stieglitz did not properly clear a significant number of his palladium prints, and, as laboratory experiments have demonstrated, improper clearing allows a large reservoir of iron to remain, eventually forming stains. The stains generated after accelerated aging are similar to those seen in many of Stieglitz’s palladium prints in the National Gallery of Art collection. If Steichen indeed used sodium acetate to reclear Stieglitz’s prints, then little residual iron was removed, despite their temporarily improved appearance.

The XRF spectra collected from the samples also demonstrate that many of the potential treatments are effective in removing some of the residual iron (see fig. 13). The amount of residual iron in samples poorly cleared by citrate or by hydrochloric acid show improvement regardless of treatment method. Even deionized water (typically slightly acidic because it absorbs CO₂ from the air to form carbonic acid) shows an ability to remove some residual iron from the poorly processed sample prints. All reclearing treatments of the aged samples, including water alone, resulted in an improved appearance, with less staining. Of all the possible treatments that Steichen could have used, the one that removes the least amount of iron is the sodium acetate alone—the very treatment Joel Snyder states that Steichen said he used. This choice of treatment provides the likeliest explanation for why Stieglitz’s palladium prints have restained despite their treatment by Steichen.

While it has been shown that the presence of residual iron induces staining in palladium prints, it is not yet understood how it causes discoloration. The presence of iron alone, most likely in the form of iron(III), does not mean a print will look stained, as evidenced by freshly created palladium prints that look well cleared but have high residual iron content. The discoloration is quite possibly due to the interaction of two iron(III) centers via an oxide bridge (Fe-O-Fe) to form binuclear metal-to-metal charge-transfer complexes that are much more intensely colored than isolated iron(III) complexes. Because some of the potential treatments remove little to no iron, the decolorization (increased whiteness of the highlights) that occurs would result from disrupting the iron-oxygen-iron bridge by a bidentate ligand such as acetate.
Consequently, the iron-oxygen-iron bridges can easily reform and the stains would reappear over time. Color measurements of the palladium simulacra show an improvement in whiteness after reclearing treatments, but all simulacra yellow to some degree following re-aging (see fig. 14). The simulacra recleared in plain water or sodium acetate, neither of which removes much iron, would likely continue to darken with continued accelerated aging more than their counterparts cleared in more effective solutions.

Conclusions
The long-term investigation of Alfred Stieglitz’s palladium prints is an example of how the chemical complexities of photographs require a broad and deep understanding of the materials and working methods of the photographer and the need for scientific study to make sound recommendations for their care. While questions remain that further research might answer, the present study has demonstrated that photographs with a reputation for permanence may be subject to deterioration if improperly processed when they were made and that chemical treatments to restore their appearance must be carefully designed to address the complex material characteristics of the photograph.

Severson quoted O’Keeffe, who referred to Stieglitz’s palladium prints saying, “Steichen does something to them that clears them, and to me it seems a good thing to do. . . . He thinks it will give the prints a much longer life.” Severson continued, stating, “Whether this statement proves prophetic or ironic remains to be seen.”

It is ironic, indeed, that despite Stieglitz’s grounding in photographic science and practice, some of his palladium prints deteriorated. In 1902, advocating for proper processing of platinum prints, he declaimed, “how important proper clearing of the platinoype is, and yet how carelessly and sloppily is this part of the process attended to by the average worker — yes, even by the best?”

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Figure 14. Graph showing ASTM E313 Whiteness Index of the third set of palladium simulacra prepared with Lake George well water. Only areas of sensitizer stain were measured. The Whiteness Index decreases for all simulacra after accelerated aging, increases to some degree after all reclearing treatments, and then decreases after re-aging. The ASTM E313-15e1 Whiteness Index is defined as

\[ W = Y + 800(0.3127 - x) + 1700(0.3290 - y) \]

where \( Y \) is the luminance, and \( x, y \) are the chromaticity coordinates of the specimen. The illuminant is D65, as defined by the CIE in 1931, and determines the constants used in the equation. On this scale, a perfect white is 100.
Stieglitz to Paul Strand, July 15, 1922, Paul Strand Collection, Center for Creative Photography, for collecting and shutting the water from Lake George to the National Gallery of Art. Finally the authors thank their families and friends for their support during this investigation.

Notes
3. For an in-depth discussion of sensitizer stain, see Matthew L. Clarke, “Characterization, Degradation, and Analysis of Platinum and Palladium Prints,” in this volume.
4. Georgia O’Keeffe to Daniel Catton Rich, January 30, 1950, Art Institute of Chicago Institutional Archives. Rich was chief curator and director of fine arts at the Art Institute at the time.
8. Stieglitz 1902.
9. Stieglitz 1892, 154: “Let me assure you that many of my prize photos, all of which are still in as perfect condition as on the day they were made, were turned out inside of fifteen minutes, including printing, developing, fixing, washing and mounting”
10. Alfred Stieglitz to Alfred Clements, December 26, 1916, Alfred Stieglitz/Georgia O’Keeffe Archive, Yale Collection of American Literature, Beinecke Rare Book and Manuscript Library, Yale University, New Haven, Conn.
11. “Palladiotype” 1917, 180. See also Mike Ware, “The Technical History and Chemistry of Platinum and Palladium Printing,” in this volume.
14. Numerous letters from Stieglitz that refer to his photographic practice are found in the Yale Collection of American Literature and in the Paul Strand Collection, Center for Creative Photography, Tucson, Ariz.
15. Alfred Stieglitz to Paul Strand, August 4, 1921, Paul Strand Collection, Center for Creative Photography. See also Greenough, “Great Day for Palladio,” in this volume.
18. Willis & Clements n.d.
19. Willis & Clements 1908, 12. See also Clarke et al. 2015.
20. Stieglitz often used the term “proof” interchangeably with “print.” “Proof” is a term that usually describes a trial print.
21. Stieglitz to Paul Strand, July 15, 1922, Paul Strand Collection, Center for Creative Photography.
22. Stieglitz to Rebecca Strand, October 22, 1923, Rebecca Salisbury James Papers, Yale Collection of American Literature.
23. O’Keeffe 1978, [5th page of unpaginated introduction]
24. Stieglitz to Paul Strand, September 2, 1922, Paul Strand Collection, Center for Creative Photography.
26. Stieglitz to Paul Strand, July 20, 1928, Paul Strand Collection, Center for Creative Photography.
27. Stieglitz to Paul Strand, October 6, 1919, Paul Strand Collection, Center for Creative Photography.
28. Stieglitz to Herbert J. Seligmann, October 14, 1921, Yale Collection of American Literature.
30. Doris Bry, interview by Constance McCabe and conservators Nora Kennedy and Nancy Reinhold, Metropolitan Museum of Art, November 28, 2001. During this interview Bry examined palladium prints by Stieglitz and shared her recollections about Steichen’s treatment and related experiences with O’Keeffe. Over two decades, Bry was extremely helpful to former Art Institute of Chicago photographer conservator Douglas G. Severson and to Constance McCabe while both periodically investigated the question of Steichen’s treatment of Stieglitz’s palladium prints.
31. Bry, interview.
33. Bry, interview. Bry stated that O’Keeffe used SpoTone, an aqueous dye for retouching photographs, to retouch the prints, but no evidence has been found of any dye-based spotting media on prints by Stieglitz. However, the media observed on Stieglitz’s prints are consistent with the opaque Eastman Spotting Colors, greasy retouching pencils, and similar media that remain in O’Keeffe’s photography retouching supplies from her studio, now in the collection of the George O’Keeffe Museum, Santa Fe, N.M., Gift of Juan and Anna Marie Hamilton.
34. A few untreated Palladiotypes by Stieglitz are in the collections of the National Gallery of Art, Museum of Modern Art, New York, and Museum of Fine Arts, Boston, and serve as valuable controls for comparison. Palladium prints by Stieglitz acquired by the Metropolitan Museum of Art in 1928 and the Museum of Fine Arts, Boston, in 1924 were among those that were not treated by Steichen.
35. Bry, interview.
37. The only known example of unprocessed Palladiotype paper is in the collection of the Museum of the History of Science, University of Oxford—“Tin Canister of Palladiotype Sensitised Photographic Paper (Grade BM),” inventory number 92955—but it was not available for research. Known Palladiotype print samples with “W & C” and “Palladio” stamped on the verso are in the William Willis file, Technical Collection, George Eastman Museum, Rochester, N.Y.; Prints and Photographs Division, lot 3222, no. 136, Library of Congress, Washington, D.C.; and Division of Photographic History, National Museum of the American History, Smithsonian Institution, Washington, D.C.
38. See Ware, “Technical History and Chemistry of Platinum and Palladium Printing,” in this volume.
40. The paper was found in existing stationery stock without any accompanying identifying information, other than the watermark, “Cranes 100% Cotton.”

41. For further discussion, see Ware, “Technical History and Chemistry of Platinum and Palladium Printing,” and Clarke, “Characterization, Degradation, and Analysis of Platinum and Palladium Prints,” in this volume.

42. Anderson 1938, 460.


44. Water Testing Laboratories of Maryland Inc. water quality report AE1105-14, May 12, 2011, states that there are 200 micrograms iron per liter of unfiltered water. A United States Geological Survey (USGS) water quality report from the Diamond Point Well (Diamond Point, New York, USGS Station Number 432902073415201), sample taken on November 4, 2009, states that there are 68 micrograms iron per liter of unfiltered water. USGS Water Data for the Nation, http://wris.waterdata.usgs.gov. The Diamond Point Well is located approximately 3 miles north of Stieglitz’s estate, Oaklawn, now The Quarters at Lake George, New York. Diamond Point Well is the source of the unfiltered well water used for this research and was provided by Kevin Delphia of Green Haven Resort, Lake George, New York, which is one-half mile north of The Quarters at Lake George.

45. It is important to note that during the normal clearing process, the residual iron(III) and excess platinum salts are removed by successive dilution in acidic baths of either citrate–citric acid or dilute hydrochloric acid. The removal of iron(III) is greatly improved by the use of acidic clearing solutions. While the palladium image metal can be attacked and dissolved by a 1:120 dilution of hydrochloric acid, even a dilution of 1:200 was not ideal for use with palladium because it still had the capacity to dissolve the low-density image. Consequently, such a weak solution of hydrochloric acid is not as effective a clearing agent as a solution of citrate, which itself is only a mild chelator.

46. Crawford 1979, 171. Crawford’s 1:60 hydrochloric acid:water clear was used to make the prints. Crawford makes no mention of using a more dilute concentration for palladium prints.

47. Beaumont Newhall to NGMA paper conservator Catherine Nicholson, personal communication, June 3, 1983: “It is my recollection that Steichen ‘treated’ the palladiotypes simply by refixing them with a 1:80 solution of hydrochloric acid, but I did not take notes at the time. . . . I must emphasize that I cannot prove that Steichen’s treatment as refixing, and that this is only my recollection.” Photograph Conservation Department records, National Gallery of Art.

48. Anderson 1938, 460. The use of hydrochloric acid as a reclearing agent in the 1993 study was based on a suggestion given by Clerc for restoring yellowed platinum prints. Clerc 1930, 389. For palladium prints, Anderson found it “convenient to clear in three successive baths of a solution of 1 to 200 hydrochloric acid in water.”

49. Plenderleith 1971, 81.


51. McCabe’s 1993 study was not published but is summarized in Severson 1995, 7–8.

52. The compound ethylenediaminetriacetic acid (EDTA) was synthesized in the 1930s in Germany by Ferdinand Münn, who obtained a U.S. patent for it in 1938. Münn 1938.

53. A Lab-Line Instruments, Inc., Orbit Shaker equipped with a rheostat was used to achieve controlled and gentle agitation.


56. Stieglitz 1902, 30.

References


