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## A Summary of Early Chemical and Physical Treatments of Platinum Prints

Erin L. Murphy

The reputed permanence of platinum and palladium prints has been questioned from the earliest days. Almost as soon as the platinum process found widespread popularity, photographers began to publish treatments and remedies for prints that had lost their initial pristine luster, and many photographers indulged in chemical and physical treatments to rectify the apparent failings of a finished platinum print. In most cases, postprocessing cleaning or other treatments were undertaken to remove surface grime or enhance the aesthetic appearance of a stained or yellowed print. In other cases, the decision to improve the appearance of a platinotype may have simply been motivated by more practical matters of business or economics.

This essay presents an overview of chemical and physical treatments used by practitioners early in the platinum era as well as a brief look at contemporary treatment practices by trained professional conservators. Presentation of these methods is not intended to endorse their use; rather, this information is presented as an aid to historians and conservators who may be confronted with the aftereffects of early treatments. Readers will note that with few exceptions the materials used for cleaning and “brightening” platinum prints were readily available in most households (fig. 1), and the practical application of these procedures did not require specialized photographic or chemical knowledge.

### Removal of Surface Dirt and Stains

The open, fibrous surface of most platinotypes, unprotected by a coating of gelatin, albumen, or other substance, was vulnerable to staining from grease or ink and the accumulation of dirt and grime from the environment. Instructions for removing dirt and grime from the surface of a platinotype took into account the delicate nature of the photograph and steered practitioners away from more abrasive cleaning materials, such as erasers or bread crumbs, traditionally used to clean the surfaces of gelatin or albumen prints.<sup>1</sup> One common dry method of cleaning was to use a lump of soft bread or stiff dough. Directions for use came from one author in the *Photographic Journal of America*, who borrowed the idea from wallpaper hangers at their work:

Before trying any other method of restoration, the first thing to be done with a print, no matter by what process it may be made, is to get rid of what may be termed adherent dirt—that is to say, dirt which cannot be removed by gentle friction with a soft rag or, better still, a pad of cotton-wool. This is best effected by gently dabbing the surface with a fair-sized lump of stiff dough. . . . The dough must be spread out and folded over as the surface becomes soiled, until the whole mass is too dirty to be of further service. . . . The dough is made of a cheap quality of flour . . . mixed with cold water and kneaded until it does not stick to the fingers. . . . The dough may be used with safety upon any print, silver, carbon, platinum, or bromide, and will often be found to do all that is necessary.<sup>2</sup>

Figure 1. Advertisement for Kifó Eau de Javel, nineteenth century. Private collection. The advertisement claims, “This product is recommended for consumers for its strength and purity. Purified and very carefully manufactured, it is superior to all other similar products.” A common household chlorine bleach, *eau de javel* was advocated for use by some early practitioners to remove yellow stains from platinum prints.

For wet cleaning, the photographer was advised to make a semifluid paste of flour, water, and a pinch of alum and to brush the mixture onto the surface of the print:

Prints on unglazed paper of rough surface are apt to become soiled and degraded by dust particles collecting in the depressions of the paper. Stretch a sheet of fine muslin over the mouth of a tub or bucket. Lay the print face down on the muslin. Pour hot water from a jug over the back of the print. Or, dissolve a pinch of alum in a cupful of cold water. Then add household flour enough to make a sticky paste. Lay the print face upwards on a sheet of glass, apply the paste to the surface with a soft brush and spread it well with the fingers. Then wash off under a gentle spray of cold water. The sticky paste carries away the dust and dirt along with it.<sup>3</sup>

Tenacious stains, such as inks or grease, could be removed with a saturated solution of oxalic acid in warm water applied with cotton wool,<sup>4</sup> or with benzole, ordinary petrol, or “motor spirits,”<sup>5</sup> or warm turpentine followed by an application of alcohol.<sup>6</sup>

### **Causes of Discoloration and the Influence of Iron**

Beyond the problem of dirt and grime on a print, photographers often remarked on discoloration, darkening, or yellowing of a platinum print. Although sometimes referred to in the literature as “fading,” early practitioners were well aware that the fault was not a loss of the platinum image but a tendency of the paper to yellow, thereby decreasing the print’s apparent contrast. In general, these photographers understood that residual iron salts played a role in yellowing but were divided on the total impact of such residues.

Several late nineteenth- and early twentieth-century chemists performed extensive tests to determine the causes of yellowing in platinum prints and published their findings in the journals of the period. Henry Chapman Jones, a chemist and member of the Royal Photographic Society, investigated the yellowing question, and his results and subsequent discussions among his peers can be found in various journals from 1887 to 1904.

Jones’s early tests established that color change in platinum prints was due in part to residual iron compounds but that the prints darkened and yellowed markedly when exposed to hydrogen sulfide.<sup>7</sup> In later tests, Jones proved that iron and platinum salts remain in the print regardless of the extent of clearing and washing. In 1901 he wrote:

In a paper read before the Royal Photographic Society in 1895 I showed that paper once coated with ferric oxalate could not be washed quite free from iron by the use of hydrochloric acid and water, and that the iron remaining was competent to produce such results as had been observed. . . . Although the iron salts can produce the observed results, the platinum salt used, when once put upon the paper, cannot be completely removed from it. . . . It seems, therefore, that in a platinum print, however carefully prepared, there is a residue of iron and of platinum compounds in some changeable form over the whole print.<sup>8</sup>

Jones also concluded that a very small amount of residual iron left in a poorly processed print was less of a concern to him than the presence of hydrogen sulfide in the atmosphere in combination with residual iron and platinum salts:

As a matter of fact platinum prints contain a little iron salt or compound associated with the platinum, and the amount of it will vary according to the care with which the print has been prepared. If properly cleared and washed, the amount will be exceedingly minute; if carelessly finished it will still be small but more appreciable. The quantity of iron left in the print by the most careless operator would, I believe, be quite without effect on the permanency of the print. But such a carelessly made print, if subjected to sulphuretted hydrogen, or in general to such circumstances that cause silver prints to fade, will turn to an unpleasant yellowish tint reminding one very much of a faded silver print.<sup>9</sup>

Other practitioners offered additional explanations for the yellowing of platinum prints. Dr. Richard Jacoby performed his own tests, but his conclusions indicated that residual platinum from the sensitizer played a greater part in yellowing than iron salts. His tests involved coating two pieces of paper, one with lead-iron sensitizer and one with potassium chloroplatinite solution. The paper containing the iron sensitizer could be fully cleared with a hydrochloric bath, but the paper coated with the platinum salts retained a distinct yellow color. Furthermore, if these two papers were kept for several months, the platinum-coated paper would turn a deep brownish yellow.<sup>10</sup> Jacoby’s findings, therefore, echoed Jones’s earlier theory that “Platinum compounds may therefore occasionally have something to do with the changes produced.”<sup>11</sup>

In addition, Jacoby noted that yellowing appeared more often on rough-textured papers than on smooth, and he challenged contemporary theories that yellowing was the result of interaction between platinum and gelatin sizing in the paper. Instead, he suggested that moisture reacting with the thin film of platinum salts on prepared papers caused a premature reduction to metal prior to exposure and development. This reduction to metal caused a darkening of the paper overall. Jacoby also advised that the traditional method of fixing platinotypes contributed to yellowing, and he instructed practitioners to treat prints with ammonium oxalate or ammonium citrate after the standard hydrochloric clearing bath.<sup>12</sup>

### Early Chemical Treatments

Regardless of the causes of yellowing, a number of treatments were recommended for removing unwanted discoloration from platinum prints. Nearly all the early treatments mentioned are variations on chemical bleaching in which a powerful oxidizer or reducer acts to break the bonds of the chromophores<sup>13</sup> responsible for the paper's yellow appearance. Unlike modern-day professional conservators, who tend to carefully weigh the benefits and risks of bleaching a paper artifact, early practitioners appeared to eagerly embrace bleaching methods originally used for the restoration of drawings and engravings. In general, the recommended bleaching recipes were some combination of calcium hypochlorite (an oxidizing bleach) and dilute hydrochloric acid. One could use these compounds singly, but the effects seem to have been enhanced with an excess of chlorine in the bath.

### Chemical Bleaching Recipes

Understanding the techniques commonly practiced by early photographers can be extremely instructional when deliberating issues regarding the preservation of a historic object. Early literature abounds with recipes for bleaching platinum prints, and such recipes persisted well into the twentieth century. The following sampling of only a few of these recipes is reproduced here as an aid to conservators or other stewards of historic photograph collections who might be called upon to revisit or unravel the past treatment history of items in their care.<sup>14</sup>

**READERS PLEASE NOTE: These recipes are not appropriate for use with photographs.** These treatments pose extreme risks to the physical integrity of the print and should not be attempted. Aside from the dangerous, often unknown, long-term risks to the photograph

from these practices, early photographers did not observe rules of health and safety common today in all scientific and conservation laboratories (e.g., smelling mixtures to determine chemical or solvent ratios is not safe!!). These archaic practices and methods should not serve as a model for current practice.

Also note that the “bleaching powder” often mentioned in the early literature is defined by E. J. Wall as “the so-called chloride of lime of the shops, the active ingredient of which is probably calcium hypochlorite, and this in contact with acids liberates the powerfully oxidising hypochlorous acid.”<sup>15</sup>

The following recipes, dating from 1897 to 1917, were specifically meant for use with platinum prints, the image of which the writers believed to be stable in these solutions. However, the oxidizing bleaches described below can have a powerfully destructive effect on some photographic images. In addition, very little cautionary advice was offered regarding the potentially damaging effects of these agents on the paper supports.

#### *Wilson's Photographic Magazine, 1897*

Often the paper support for the platinotype image yellows with age or impurities. As, however, the image itself is unaffected by the action of bleaching powder, the stain may be removed by soaking the damped print in a 2½ per cent. solution of so-called chloride of lime for ten minutes, then removing the print, and after adding to the bath twelve drops of hydrochloric acid replacing it. If the stain is very obstinate, the latter part of the process must be repeated from time to time. A thorough washing is subsequently necessary.<sup>16</sup>

#### *Photographic Times-Bulletin, 1902*

Platinum pictures have the reputation of complete durability. Still an old platinum picture may have a more flat appearance than one newly made. . . . Traces of iron or platinum salt remain, which in the course of time, when thoroughly dried up, effect the yellow coloration. A simple immersing in an aqueous solution of hypo-chloric acid, acidified with muriatic acid, produces at once again the pure white paper support. Bathing of the finished picture in citrate of ammonia is always advisable, after the muriatic acid has been removed by washing. Then wash again in pure water and dry in the open air.<sup>17</sup>

### *Practical Photographer, 1904*

Immerse yellow-stained prints in a 5 per cent solution of oxalic acid and wash well afterwards.<sup>18</sup>

### *Complete Photographer, 1906*

Mr. Chapman Jones has recommended a solution of hydrochloric acid, one part of acid to twenty of water, to which has been added a few drops of a solution of sodium hypochlorite. Enough of this should be poured in to give the mixture a distinct smell of chlorine. Those who do not know what the smell of chlorine is like need not regard this as an insuperable difficulty. They can add the hypochlorite until they can smell something else besides the hydrochloric acid, and that will be chlorine. They will thus learn what chlorine does smell like, an increase of knowledge not accompanied by that increase of pleasure which is generally supposed to repay intellectual acquisitions. The print is placed in this liquid until it has reassumed its original condition, after which it is washed and dried.<sup>19</sup>

### *Photographic Journal of America, 1917*

Platinum prints are more delicate subjects, and will not, as a rule, stand any friction. In most cases the dough treatment will be sufficient, but if there be a considerable amount of yellowing a clearing bath of hydrochloric acid may be found necessary. If the stain does not yield to the acid, a bath of diluted “eau de javelle” [common chlorine bleach] will usually answer. It is necessary to be very cautious when using this, or a weak solution of chloride of lime as there is a tendency to rot the paper. Immersion in a 5 per cent. solution of hypo will neutralize the chlorine and will not injure a platinum image.<sup>20</sup>

### **Color Reversion after Bleaching**

Early practitioners appeared to be largely unconcerned with the long-term effects of bleaching prints, and they considered the practice of chemically “brightening” a print as an appropriate and admirable end in itself. With few records kept regarding postprocessing bleaching or other treatments during this time period, it is impossible to truly understand the impact of these practices over time. It is useful to note, however, that practitioners were aware that bleaching did not offer a permanent solution to the problem of yellowing, as the discoloration would return over time. Jones remarked, “Nor does the chlorine treatment

confer immunity from change by sulphuretted hydrogen, for prints that have been browned by it and then bleached and washed are apparently as readily affected by it again as at first.”<sup>21</sup>

### **Contemporary Conservation Treatments and Research**

Contemporary conservation treatments have changed greatly since the late nineteenth and early twentieth century, leaving hydrochloric acid baths and flour-dough cleaners behind as charming artifacts of photographic history. While conservation treatment practices have evolved over time, the professional field of photograph conservation is still quite young. The design and implementation of conservation treatments increasingly rely on scientific research, collective experience, and collaborative exchange of knowledge, as well as a growing understanding of the importance of each artist’s intent in creating a print.

Evidence of a heightened appreciation of the chemical complexity of platinum prints and an increased sophistication of conservation treatments of platinum prints are found in publications of the late 1970s and early 1980s. Treatment protocols of that time generally involved less aggressive approaches, such as gentle surface cleaning with kneaded erasers and a reducing bleaching protocol consisting of a series of baths using a balanced alkali solution and a sodium metaborate compound. If necessary, local oxidizing bleaching was carried out with a 0.1% calcium hypochlorite solution at pH 8.5 followed with a water rinse, immersion in an antichlor to remove the bleaching agents, and several series of final water baths.<sup>22</sup>

Significant leaps of scholarship in regard to the study of platinum prints occurred in the late 1980s and mid-1990s with the publication of research by Mike Ware, Douglas G. Severson, Adam Gottlieb, Constance McCabe, and Lisha Deming Glinsman.<sup>23</sup> These articles looked more closely at the history of platinum and palladium printing and added greatly to our understanding of the platinum and palladium processes, particularly as it applied to the work of Alfred Stieglitz (1864–1946).<sup>24</sup>

Two more recent treatment-related studies include those of Megan Gent and Jacqueline Rees in 1994 and Michelle Phillips in 2001. In 1993 Gent and Rees set out to find a practical conservation treatment for removal of residual iron using the chelating agent ethylenediaminetetraacetic acid (EDTA) in conjunction with sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ). Four mounted platinum study prints with yellowing and staining were chosen for treatment. Initial testing showed that three of the four prints

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contained “significant” amounts of iron. The prints were first immersed for 20 minutes in a bath of 2% w/v sodium dithionite solution adjusted to pH 6.5. This treatment showed minimal improvement, so the prints were reimmersed in an 8% dithionite-EDTA solution adjusted to pH 8.5 for much longer periods of time, up to 22 hours. Longer immersion times resulted in a dramatic improvement in appearance of the prints with a reduction in both foxing and yellowing. Subsequent analysis of the prints with energy dispersive x-ray fluorescence spectroscopy (EDX-RF) showed that approximately 80% of the residual iron had been removed. However, although the authors concluded that this treatment was a successful method of removing iron, they cautioned that it had also removed all the calcium and zinc fillers in the paper. In addition, they remarked that it was not possible to ascertain how much the decrease in yellowing was a result of removal of residual iron and how much was due to the bleaching effect of the sodium dithionite solution. The inevitable color reversion over time was also noted by the authors.<sup>25</sup>

Research by the paper conservator Michelle Phillips published in 2001 took a closer look at the effects of aqueous immersion washing treatments on platinum photographs. Her research focused specifically on the effects of water immersion on the image-forming materials and the relationship between the platinum and the paper support. Phillips created print mock-ups from a standard recipe and artificially aged the samples to promote yellowing. The aged samples were then immersed in distilled water for 30–180 minutes. Pre- and posttesting densitometry, combined with scanning electron microscopy and energy dispersive x-ray analysis (SEM-EDX) revealed that platinum image metal was redistributed during the immersion wash, particularly within the first hour. Based on the results of this research, Phillips concluded that platinum does not exist as discrete conglomerations of particles residing in the interstices of the paper matrix but that platinum particles exist overall on the print and paper fibers. As a result, expansion and contraction of the paper fibers during immersion in water may cause a disruption and redistribution of the image particles and a concurrent increase or decrease in density.<sup>26</sup>

### **An Informal Survey of Treatment Practices**

In preparation for the research reported in this essay, a small informal poll was taken among photograph conservators working in private practice and regional centers regarding conservation treatment protocols for platinum prints. It provides a useful snapshot of the state of conser-

vation practices today. As a group, the respondents seemed to treat fewer platinum prints than in former years, and those that do keep treatments minimal whenever possible. Blotter washing, rather than immersion washing, is preferred, and if bleaching is deemed necessary, the conservators use artificial or natural light bleaching rather than chemical bleaching. The use of chelators, such as EDTA, and chemical bleaching agents was extremely rare, perhaps due in part to unknown long-term effects. In the case of one respondent, x-ray fluorescence spectroscopy is currently being employed to check levels of iron in the platinum print before and after treatment.

### **Conclusions**

This research makes it very clear that the chemical lives of photographs continue long after they leave the artists’ studios. Any number of additional chemical treatments and additives may have been applied to a print, perhaps many years after its initial production and for reasons quite unknown to the contemporary viewer. Early literature with references to solvent cleaners or chemical bleaching techniques provides a wealth of information that can help guide current and future preservation practices, but without the recorded instances of bleaching or other treatments on photographs within a collection, it is difficult to track the long-term impact of these practices.

For conservators facing the complexities of preservation and treatment, it is crucial to understand the range of materials that may have been applied to prints earlier in their existence. Truly informed decisions regarding the care of platinum prints can be achieved when conservators, scientists, and historians work together to understand the methods and aesthetic goals of individual artists, to gather knowledge of prior treatment practices, and to utilize the sophisticated analytical and monitoring equipment intended to describe the material characteristics of photographs. As our understanding of early photography advances, our combined knowledge can be used in the contemplation of treatment, exhibition, and use of these extraordinary objects.<sup>27</sup>

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protocols. My appreciation to the preservation, cataloging, and curatorial staff at The New York Public Library and at the Weissman Preservation Center at Harvard Library. Finally, this project was realized in great part due to many institutions that have made access to early photographic periodicals possible through various digitization initiatives. The cooperative efforts of such entities as Google and the Hathi Trust, for example, with cultural institutions such as The New York Public Library, Harvard Library, Colgate University Library, and the University of Michigan in particular made this research possible.

## Notes

1. [Watkins] 1917, 399.
2. [Watkins] 1917, 398.
3. [Cummings and Lambert] 1904, 62.
4. [Ward] 1899, 279.
5. [Watkins] 1917, 398.
6. Burton 1904, 35.
7. Jones 1895, 263.
8. Jones 1901, 444.
9. Jones 1904, 46.
10. [Wilson] 1901, 453.
11. Jones 1895, 263.
12. [Wilson] 1901, 453.
13. Chromophores are a group or groups of atoms within a molecule that are responsible for the color of a material, as interpreted by the human eye.
14. The following offer an additional sampling of bleaching recipes of the late nineteenth and early twentieth centuries: Wall 1902, 84; Walton 1904, 37, 38; [Bartlett and Chambers] 1913, 785; [Ward] 1899, 279; Wenzel and J.C.A. 1902, 264; Jones 1901, 444; [Tennant] 1902, 289.
15. Wall 1902, 84.
16. Warren 1897, 473-74.
17. Dietrich 1902, 497.
18. Burton 1904, 35.
19. Child Bayley 1906, 204.
20. [Watkins] 1917, 399.
21. Jones 1895, 263.
22. Norris 1979, 74; Norris 1980, 58.
23. Ware 1986; Severson 1995; Gottlieb 1995; McCabe and Glinsman 1995.
24. An expanded discussion of Stieglitz's work and Steichen's treatment can be found in Constance McCabe et al., "Alfred Stieglitz's Palladium Prints: Treated by Steichen," in this volume.
25. Gent and Rees 1994, 94-95.
26. Phillips 2001. For additional discussion of the morphology of image-forming platinum material, see Matthew L. Clarke and Dana Hemmenway, "Investigating Chelating Agents for the Treatment of Platinum Prints," in this volume.
27. For additional discussions of treatment and preservation, see McCabe et al., "Alfred Stieglitz's Palladium Prints," Clarke and Hemmenway, "Investigating Chelating Agents," and Jennifer Jae Gutierrez, "Caring for Platinum and Palladium Prints: Storage and Display," in this volume.

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