Investigating Chelating Agents for the Treatment of Platinum Prints

Matthew L. Clarke and Dana Hemmenway

The formation of stains in platinum and palladium prints has been discussed at length in this volume. This gradual formation of yellow discoloration is often caused by the presence of residual iron (Fe(III)) in the print due to incomplete clearing of the iron-laden sensitizer. Removal of iron from these prints can improve the image and reduce further staining. One such method is the application of chelators.

The use of chelators for paper conservation applications was first discussed by Helen Burgess in 1991.[1] Since then more studies have been conducted to understand the corrosive action of metal complexes, such as iron gall ink and copper pigments. To date, however, only Megan Gent and Jacqueline Rees in 1994 have published a study that directly involves chelating iron stains in aged platinum prints.[2] The present study was initiated to better understand the implications of chelation treatments as they impact the long-term stability of platinum prints.

Three chelators were chosen to test their effectiveness in reducing iron-related stains based on their prior use in the field of conservation: ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), and the more recently introduced N,N′-di(2-hydroxybenzyl) ethylenediamine-N,N′-diacetic acid (HBED). The chelators increase in cost and decrease in solubility in this order: EDTA, DTPA, and HBED.

Poorly processed platinum prints were prepared and subjected to accelerated aging to produce stains (fig. 1).[3] These prints were then subjected to a range of treatment agents and conditions: varying chelation time, concentration, pH, the presence and amount of a reducing agent (sodium dithionite), and the washing time after treatment. Control samples were retained, and portions of these prints were subjected to further accelerated aging. The prints were examined by colorimetery to quantify the color change and x-ray fluorescence analysis to determine the reduction in residual iron. Figure 2 illustrates one sample set, chelated by variants of EDTA, and is representative of the many combinations tested.

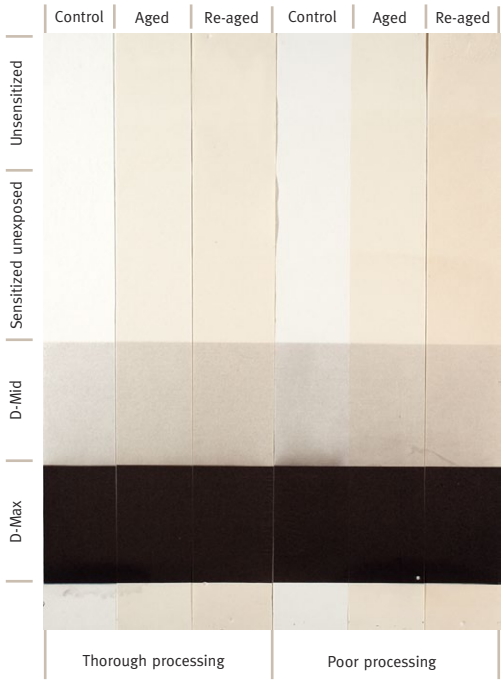

Figure 1. Platinum print step-tablets prepared at the National Gallery of Art using ferric oxalate and potassium tetrachloroplatinate. The prints were either thoroughly processed (left set) or poorly processed. After repeated cycles of accelerated aging, both sets show discoloration, with the poorly processed prints yielding more dramatic staining.

All chelators successfully removed some of the iron in the prints and decreased the yellow appearance. When viewed after accelerated aging, however, the visual improvement was less apparent. Most notably, very long

Figure 2. Poorly processed platinum print step-tablets subjected to EDTA chelation. The images are cropped to focus on the sensitizer stain. The poorly processed print was artificially aged and subjected to a range of chelating variables, then finally re-aged. The samples above, grouped in pairs, show the print after chelation and after being re-aged.

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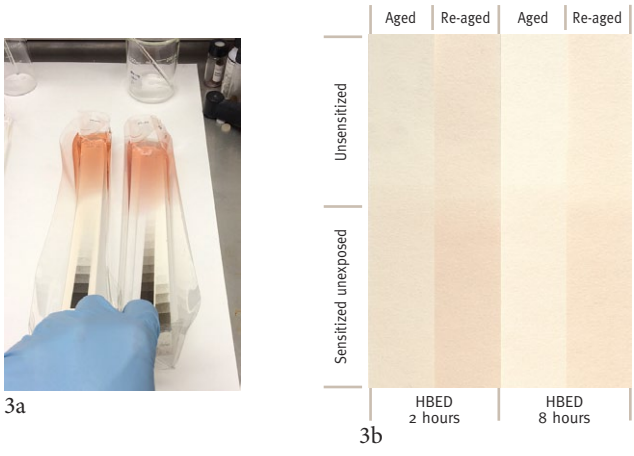
chelation times, especially with sodium dithionite, often produced prints that initially appeared brighter but exhibited a darker appearance after accelerated aging when compared with their counterparts that were chelated for shorter times.

HBED has the advantage of a very strong complexation with Fe(III), the primary component of the stains.[4] However, its low solubility at pH 8 (or lower) makes its complete removal challenging. More alkaline solutions were not tested, as only mild pH conditions (pH 6–8) were considered for these conservation tests. While prints visually appeared free of residual HBED after washing, they exhibited a pink tone after aging (fig. 3). Much longer washing times were required to remove HBED from the prints (more than 20 hours). It is important to note that this pink color was barely visible before accelerated aging.

Finally, a test was performed on a historic print from author Dana Hemmenway's study collection (fig. 4). The print was split into thirds with two portions subjected to chelation: one portion by EDTA and one by DTPA (with sodium dithionite). The yellowness of the print was reduced, as was the iron content. While all portions of the print yellowed after accelerated aging, the areas of the print that had been treated yellowed less. When these two chelation methods were compared, it was found that the DTPA treatment removed more iron while minimizing the loss of calcium from the paper compared with the EDTA treatment. Additionally, the DTPA-treated section exhibited a warmer tone compared with the cooler appearance of the EDTA-treated section.



3a 3b

Figure 3. An example of a study of HBED.

3a. HBED complexes with iron give rise to a pink-colored solution during treatment.

3b. Platinum print step-tablets made by the Photograph Conservation Department, National Gallery of Art. After washing, the prints appear to be mostly clear of HBED. After accelerated aging, however, the prints exhibited a pink tone because small amounts of HBED remained in the paper and complexed with the iron during aging.

Figure 4. Photographer unknown, [*portrait of a woman*], c. 1900. Platinum print, 12.6 × 8.6 cm. Dana Hemmenway personal collection. This chelation study shows a platinum print treated by DTPA (left) and EDTA (right), with an untreated section in the middle. After treatment the print was split, and the lower half was subjected to accelerated aging. The untreated area darkened significantly. The treated areas of the print did exhibit some darkening and yellowing, but not to the degree of the untreated area.

All chelated prints also exhibited a loss of calcium, a component of the paper support that is generally considered beneficial. A reduction in calcium could impact the aging of paper. This cautionary tale forewarns conservators to consider the long-term impact of any treatment on the object, as similar staining may appear years or decades after treatment.

Notes

1. Burgess 1991.

2. Gent and Rees 1994.

3. See Matthew L. Clarke, "Characterization, Degradation, and Analysis of Platinum and Palladium Prints," in this volume.

4. Eplattenier et al. 1967.

References

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