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### **Historical Bleaching of Ingres Drawings at the Fogg Art Museum<sup>1</sup>**

The Fogg Art Museum has the largest collection of drawings by Jean-Auguste-Dominique Ingres outside of France. They were created between 1804 and 1865, years that witnessed a major transformation of papermaking. Before this time, papers were made exclusively by hand using fermented and beaten linen rags, but a growing shortage of good quality rags led to a search for alternate fibers. By the later nineteenth century, papers were also being made by machine from linen and/or cotton mixed with cheaper fibers like straw and wood. These changes and the introduction of acidic alum-rosin sizing caused a decrease in paper quality during the nineteenth century that is reflected in Ingres' drawing papers and may have contributed to their current darkened appearance. In the middle of the twentieth century, conservators and scientists at the Fogg Art Museum employed several chemical-bleaching methods to reduce the staining in these drawings. This research focuses on the possible connection between the current darkening and previous conservation bleaching treatments, and evaluates two methods for detecting bleaching residues in paper. A brief history of paper conservation at the Fogg will serve as an introduction to this topic.

In 1927 the Fogg Art Museum opened a new building under the director, Edward Waldo Forbes, and his assistant Paul J. Sachs. Forbes was committed not only to collecting art, but to understanding the techniques and materials of artworks. To support research in this area, he created the Department of Technical Studies in 1928. Originally there were two staff members: George Stout, an art historian and conservator, and Rutherford John Gettens, a chemist (Fig. 1). In the early 1930s Evelyn Ehrlich and Minna Horwitz (Fig. 2) began volunteering in the Department of Technical Studies, working on projects such as research into the moisture permeability of surface coatings, oxidation of cellulose by bleach, prevention of mold in adhesives, and the transfer of Asian wall paintings. These women can be considered the earliest paper conservators at the Fogg, though no one specialized in one discipline as we do now.

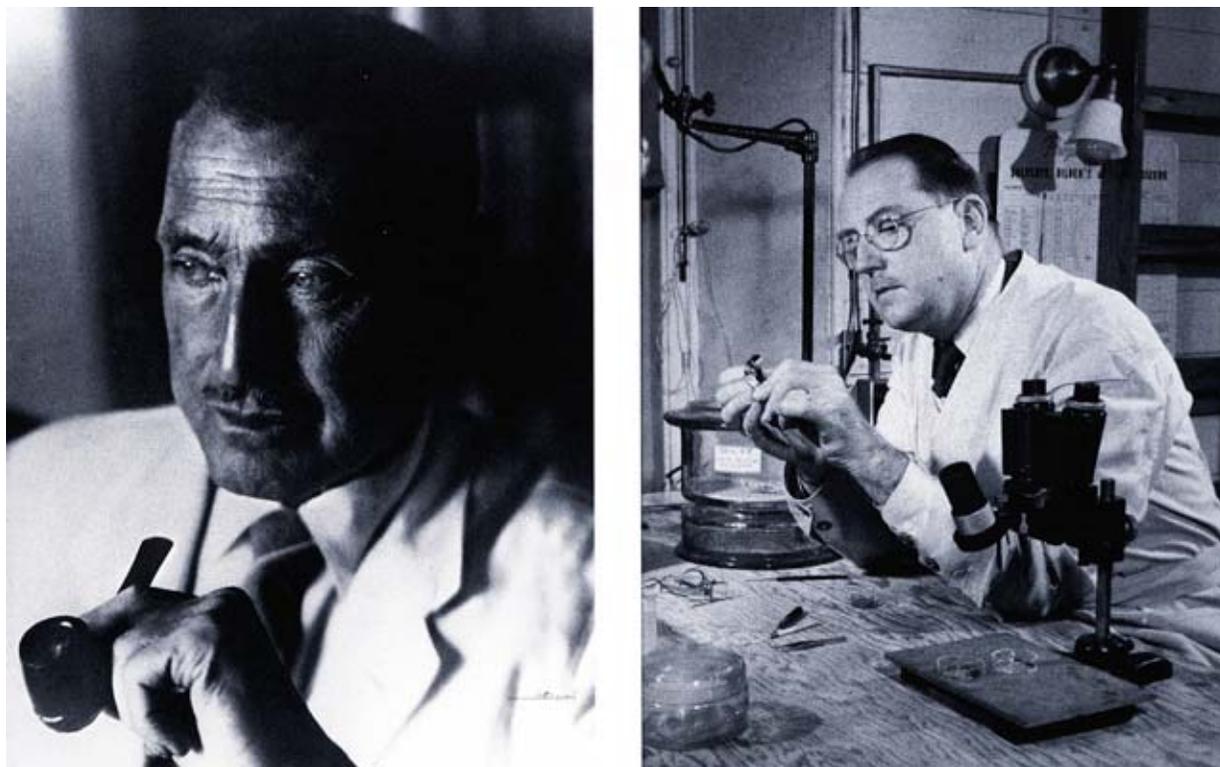


Fig. 1 George Stout, Head of Conservation 1927-1947 (left), Rutherford John Gettens, Fogg Chemist, 1928-1951 (right). ©HUAM Archives

Better known for his work on the corrosion of ancient Chinese bronzes, in 1950 John Gettens began investigating the bleaching of artworks on paper. With characteristic thoroughness, his goal was “to establish comparative data on the effect of bleaching agents on the strength and permanence of paper”<sup>2</sup> by testing nine bleaches: sodium hypochlorite, chlorine dioxide gas, sodium chlorite, chlorine gas, chlorine dioxide in water, alcohol or organic solvent, chloramine-T, hydrogen peroxide, sodium peroxide, and ozone. He was particularly interested in exploring sodium chlorite bleaching because of paper industry claims that it was less damaging to cellulose than sodium hypochlorite, which had been used at the Fogg Art Museum since 1937. The industry studied sodium chlorite for use during the bleaching of paper pulp, but unfortunately, there was no data on its behavior on already formed sheets of paper. Gettens contacted the Mathieson Chemical Corporation for help. Mathieson donated sodium chlorite for Gettens’ use, but did not have the facilities to perform the bleaching tests requested.<sup>3</sup> The chemists in their Chlorite Division told him “no rinse or wash is actually needed. However reversion of color is apt to take place due to the oxidized end products still remaining in the paper which may necessitate later bleaching. Please understand this reversion might take quite a long time.”<sup>4</sup>



Fig. 2 Evelyn Ehrlich, Conservator 1934-1948 (left), Minna Horwitz, Conservator 1931-1949 (right).  
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Based on discussions with chemists at Mathieson and his own experiments, Gettens developed three methods of bleaching with chlorine dioxide gas using sodium chlorite. These bleaching methods were extensively tested on Whatman filter paper and blank ledger paper. Physical testing of the samples was carried out at the U.S. Testing Company and at the Mellon Institute of Industrial Research under Dr. Robert Feller.<sup>5</sup> The first method generated chlorine dioxide gas in aqueous solution by combining sodium chlorite with either formaldehyde, formic acid or hydrochloric acid. He found that the bleaching results were similar regardless of how the bleach was generated. The art work was immersed in this solution followed by rinsing, similar to the hypochlorite bleaching then in common use. The second method involved a complex set up for making chlorine dioxide gas and running it through water to infuse the water with the gas. (Fig. 3) The artwork would be immersed in this solution and then rinsed.

The final method was only recommended when the artwork could not be immersed in bleach and rinsed afterward. It was to expose the artwork to chlorine dioxide gas in a bleaching chamber (Figs. 4-5) The gas was generated in the flask in the upper left in the diagram, and then passed through tubing into the sealed chamber at the bottom. The additional flask was for

neutralization of the gas. These images are from glass slides made to illustrate Gettens' research and used for teaching in the Fine Arts Department at Harvard.

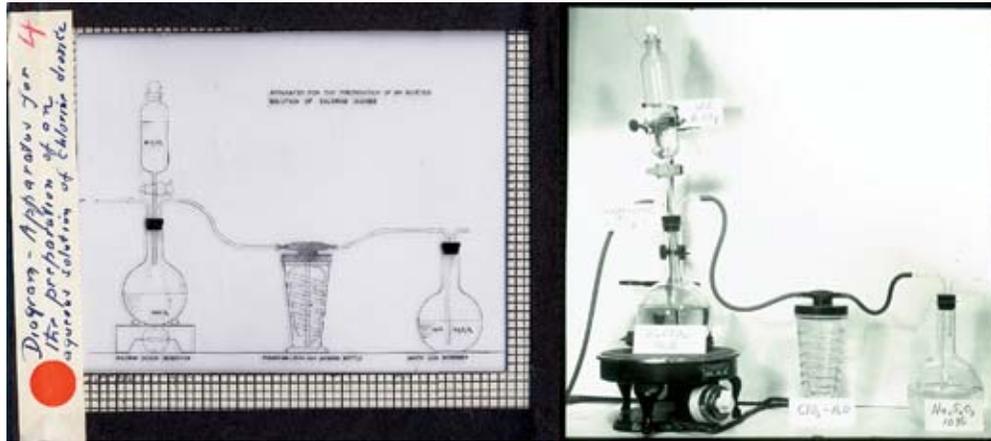


Fig. 3 Schematic drawing (left) and laboratory set up for infusing water with chlorine dioxide gas (right).  
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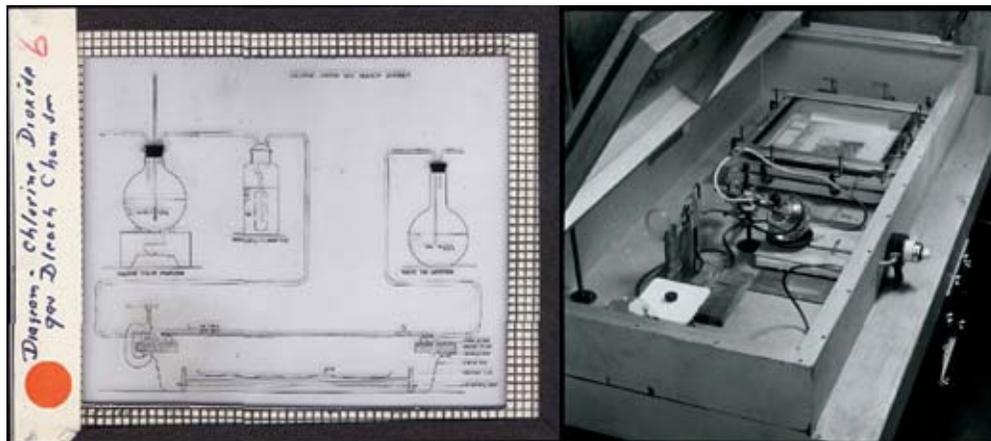


Fig. 4 Schematic drawing (left) and laboratory set up of chlorine dioxide gas bleaching chamber (right).  
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During his research, Gettens tested the bleaching effect of chlorine dioxide gas on wet and dry papers, dyed test papers, foxed ledger paper, Japanese woodblock prints, hand colored French prints, book pages, newsprint, fragments of illuminated manuscripts and plain parchment, adhesives, bistre, sepia, iron gall and other inks, red chalk, lead white and watercolor samples (Figs. 6-7). He found that the bleaching was more effective when the paper was damp or wet, that vellum and casein turned a pinkish color, iron gall ink and the other inks feathered and bleached, and the gas completely bleached out certain pigments, especially yellows and reds. Therefore, this bleach was only recommended for black and white prints and drawings.

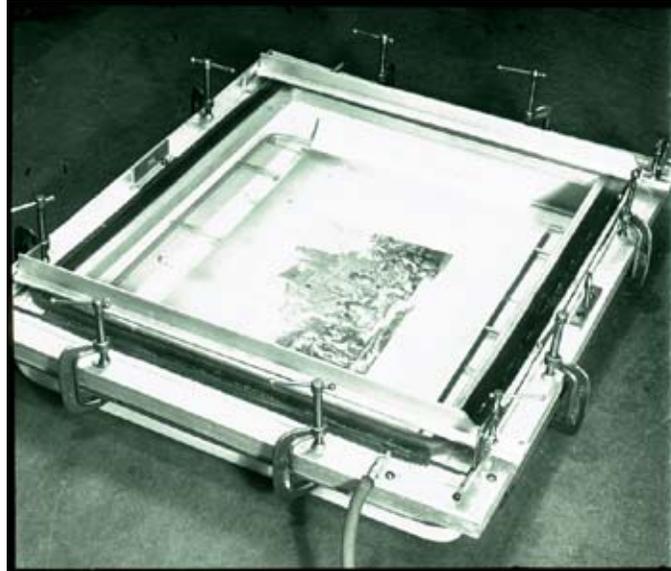


Fig. 5 Close-up view of the bleaching chamber with a print inside. ©Straus Center for Conservation, HUAM

Finally, Gettens began his “Chlorine Dioxide test run on valuable drawings.”<sup>6</sup> (Fig. 7) These “badly discolored, but important drawings” included a drapery study by Ingres, drawings by John Ruskin, Toulouse Lautrec, Bronzino, and a drawing on loan to the Fogg attributed to Tiepolo.



Fig. 6 Pages from Gettens' bleaching notebook, chlorine dioxide gas bleaching tests on Winsor & Newton's Artists' Water Colours, May 7 1951. ©Freer Gallery of Art

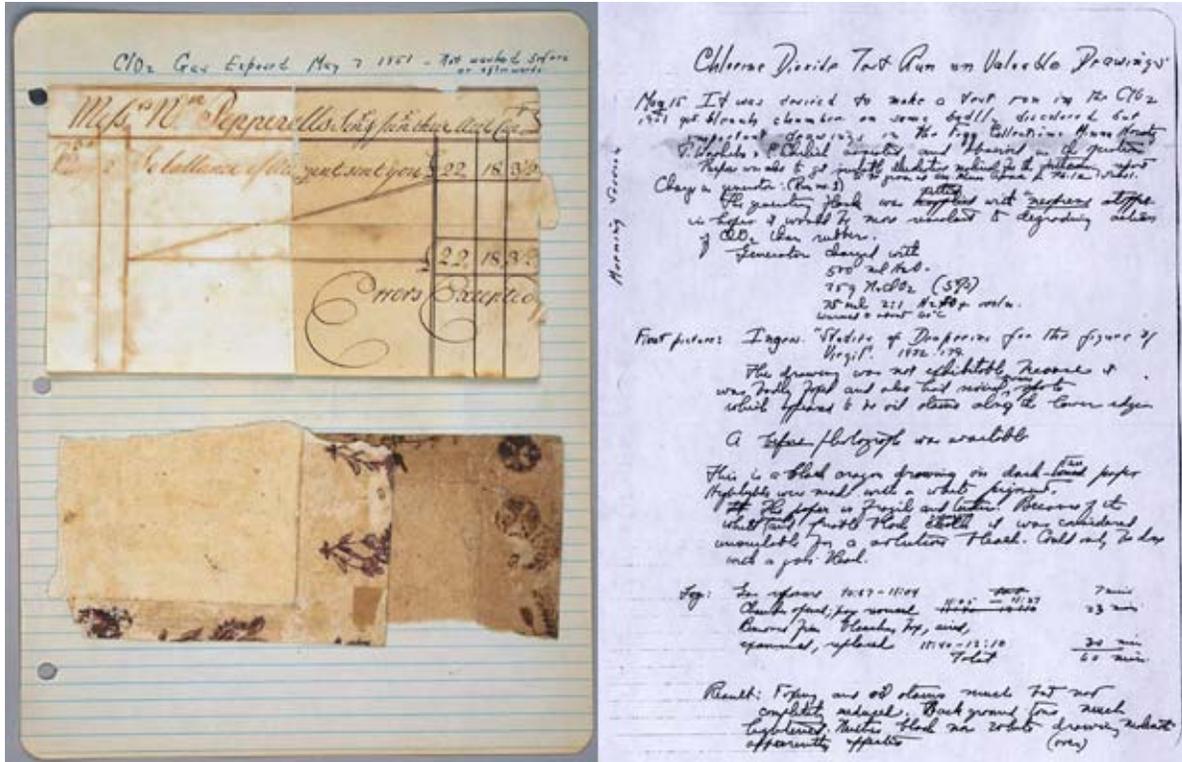


Fig. 7 Pages from Gettens' bleaching notebook, chlorine dioxide gas bleaching test on iron gall ink, May 7, 1951 (left), chlorine dioxide test runs on valuable drawings May 15, 1951 (right). ©Freer Gallery of Art

Utilizing the glass slides, original treatment files and photographs where available, and Gettens' bleaching notebook, about thirty Ingres drawings in pencil and black chalk treated between 1946 and 1953 were examined. The drawings have various forms of discoloration that have resulted from a combination of light exposure, poor quality matting and framing materials, local treatment with bleach and other chemicals, chlorine residues, and color reversion after bleaching. Ingres' drawing, *Study for the drapery of Virgil in the 'Apotheosis of Homer,'* a study for the painting in the Louvre, is a good example of the complex sources of discoloration (Fig. 8). On the left is a before treatment image of the drawing from 1932 and on the right an after treatment image from 1951. The edges of the images are irregularly cropped by the black tape sealing the slides. In Gettens' bleaching notebook he described the condition of the drawing and the reasons for its treatment. "The drawing was not exhibitable because it was badly foxed and also had several brown spots which appeared to be oil stains along the lower edge... Because of the white pigment and friable black chalk it was considered unsuitable for a solution bleach. [It] could only be done with a gas bleach."<sup>7</sup> The drawing was exposed to chlorine dioxide gas for 60 minutes after which he noted, "Foxing and oil stains much but not completely reduced.

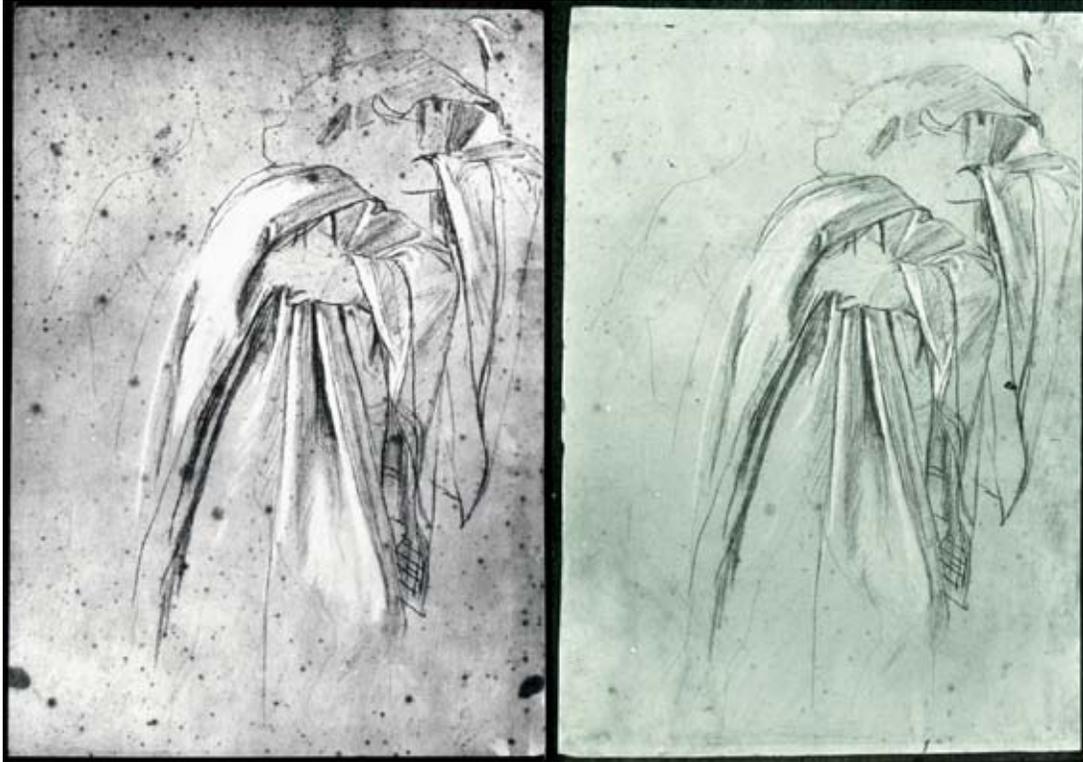


Fig. 8 J.-A.-D. Ingres, *Study for the drapery of Virgil in the 'Apotheosis of Homer,'* c. 1847, black and white chalk over graphite on tan wove paper. Harvard University Art Museums, 1932.179. Before treatment condition 1932 (left), after treatment condition 1951 (right). ©Straus Center for Conservation, HUAM

Background tone much lightened. Neither black nor white drawing material apparently affected. M. Horwitz did some additional hand work on the larger stains.”<sup>8</sup>

In fact, the drawing was later returned to the chamber for further bleaching. Even so, two months later it was brought back to the Department of Conservation and Technical Studies because “dark spots had reappeared all over the drawing. [The] cause of this reoccurrence could not be explained. Spots coincided with some of the spots in the before treatment photograph - ...but not all – and they were different in shape.”<sup>9</sup> Gettens surmised that the spots had previously been treated locally, and that the chlorine dioxide gas reacted with these local treatment areas. The current appearance of the drawing is shown in Figure 9.

As Gettens noted, many areas of foxing were replaced by halos of darker paper, which probably darkened from local bleaching without rinsing. At the lower left and along the right edge, the paper is very mottled in tone. This is visible in the 1951 after treatment slide and was the result of the “additional hand work” mentioned in Gettens’ notes. The light marks in the upper corners are from the hinges on the back. The pale vertical line at the lower right edge is a repaired tear which is visible in the 1951 slide. Today the back of the paper is cream, not



Fig. 9 J.-A.-D. Ingres, *Study for the drapery of Virgil in the 'Apotheosis of Homer,'* c. 1847, black and white chalk over graphite on tan wove paper. Harvard University Art Museums, 1932.179. The drawing in 2007, front view (left), back view (right). ©Straus Center for Conservation, HUAM

darkened by light exposure like the front. Originally, the paper would have been a tan or dark cream color, to provide a middle tone for the black and white chalk drawing. The locally bleached foxing stains are visible as brown spots on the reverse, and the white chalk highlights show as lighter areas where the calcium carbonate in the chalk protected the paper from darkening. The condition of the white chalk itself is another question. Today the dry chalk strokes are not very visible and appear to have sunk into the paper, though Gettens clearly went to great lengths not to immerse the drawing. During a preliminary presentation of this research to staff at the Fogg Art Museum, it was discovered that a bleaching treatment was performed in the mid-1960s at the request of the curator, Agnes Mongan. The paper had become very dark brown and Ms. Mongan requested that paper conservator Jerry Cohn bleach the drawing before it went on display in the Ingres Centennial Exhibition in 1967. The drawing was immersed in sodium hypochlorite bleach and rinsed in a water bath. Though treatment documentation photos have not been found for comparison, Ms. Cohn believes the paper has not darkened again, but has maintained the tone she achieved by bleaching.<sup>10</sup>

A brief review of bleaching chemistry may help explain the spread of the foxing spots and why the paper darkened after the original chlorine dioxide gas bleaching treatment. Bleaching lightens paper by changing the chemical structure of the chromophores, or the

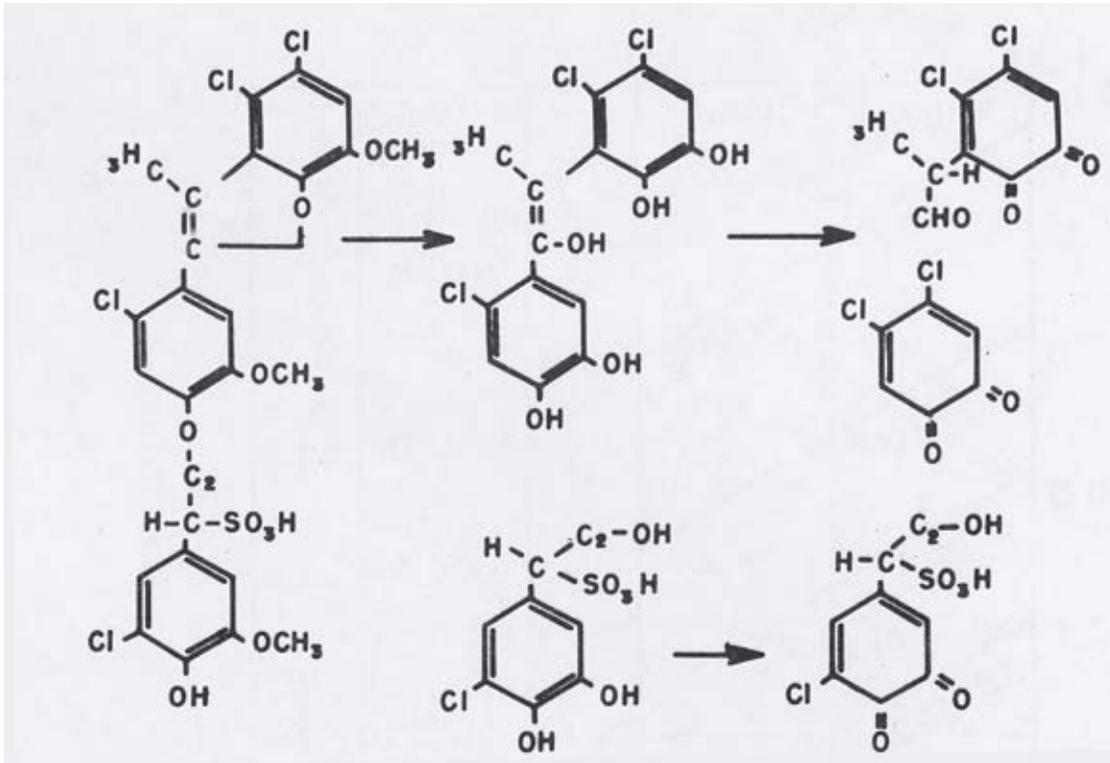


Fig. 10 Oxidation of chromophores by chlorine in aqueous solution.  
Adapted from Robert Feller, IIC-AG 1971.<sup>11</sup>

coloring matter, present. The term ‘chromophore’ refers to many dissimilar molecules that share one feature: conjugated bonds that cause them to be colored. Conjugation is the repeating single-bond, double-bond pattern [-C=C-C=C-] seen in the ring system of the sulphite lignin fragment in Figure 10.<sup>11</sup> A very simplified explanation of the diagram is that most bleaching breaks conjugated bonds through oxidation, creating smaller, non-colored molecules that are soluble in alkaline solutions. If this material is not removed from the paper, over time it can reform into another conjugated system that is colored. It may not form the previous chemical structure, which is why the darkening may appear different than the original stain. This phenomenon is often generically called color reversion, though as explained, it may actually be a color conversion. Briefly stated, the problem of color reversion underlies the need for rinsing after all bleaching treatments.

Gettens presented the preliminary results of his experiments at the American Association of Museums meeting in Philadelphia in May 1951. In correspondence with the chemists at Mathieson, Gettens said “I am reluctant to burst into print just yet before my colleagues have had a chance to try out the process in other laboratories”<sup>12</sup>, but he didn’t think he could return to this research. “Bleaching of Stained and Discoloured Pictures on Paper with Sodium Chlorite and Chlorine Dioxide,”<sup>13</sup> was published in the journal *Museum* shortly after he left the Fogg to work at the Freer Gallery of Art. From research in the Fogg conservation files, it appears that chlorine dioxide bleaching was only used during the period of Gettens’ experiments from 1950 to 1951. In all, about 25 prints and drawings were bleached using his three methods. Of the Ingres drawings examined, only three were bleached with chlorine dioxide gas. The complicated apparatus for generating the gas and the danger of an explosion were probably responsible for this bleaching method’s falling into disuse at the Fogg after Gettens left. The most commonly used bleach at the Fogg Art Museum was sodium hypochlorite, probably introduced by George Stout. It was first used in 1937 and every paper conservator through Jerry Cohn and Craigen Bowen employed it. Eleven of the Ingres drawings examined were bleached with sodium hypochlorite; two were bleached with chlorine dioxide gas and then bleached with sodium hypochlorite when the gas proved ineffective. In 1950 Chloramine-T appeared in the treatment records and was used until the mid 1970s. Four Ingres drawings studied were bleached with Chloramine-T. Overall, there was no obvious correlation found between the current color of the drawings and the types of bleach that were used. In general, the older papers were lighter than the later papers, which may relate to the changes in paper manufacture mentioned earlier.

Another aspect of this research project was to determine if bleaching residues could be detected in paper using analytical instrumentation. Bleached paper samples prepared for previous research<sup>14</sup> were used. Seven papers from the eighteenth, nineteenth and twentieth centuries, including Whatman filter paper, were bleached with Chloramine-T, an oxidizing bleach that lightens by the same mechanism as sodium hypochlorite. Samples were bleached in two ways: brushed with 2% Chloramine-T several times without rinsing, or immersed in a 2% solution and then rinsed.

Scanning Electron Microscopy (SEM) and X-Ray Fluorescence Spectroscopy (XRF) were tested for their effectiveness in detecting chlorine in paper and their appropriateness for use on artworks.<sup>15</sup> SEM analysis requires that a sample be placed in a vacuum chamber, limiting its

use with artifacts, though small artworks may be analyzed in low-vacuum SEM chambers. Kathy Eremin, Conservation Scientist at the Fogg Art Museum, analyzed these samples in the facilities of the Museum of Fine Arts, Boston. Chlorine was detected in the samples, and images of the paper surface helped locate and identify possible bleaching residues embedded in the fibers, such as sodium chloride and potassium salts (Fig. 11).

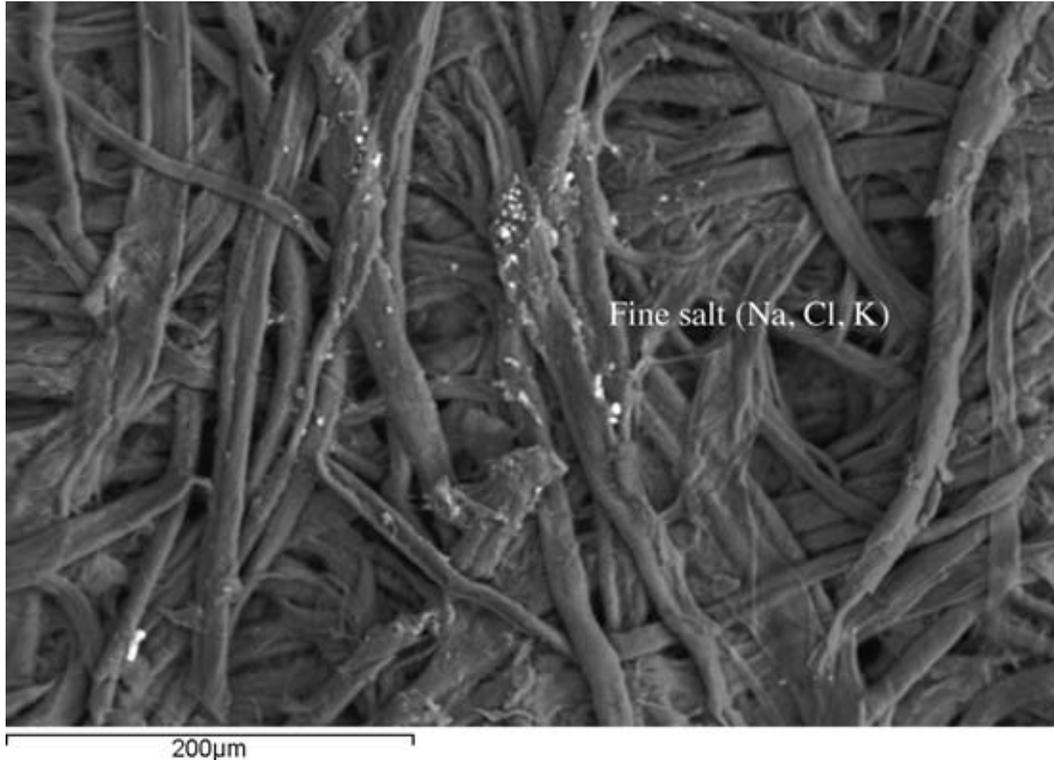


Fig. 11 SEM image of handmade, nineteenth century, gelatin-sized Whatman watercolor paper, after bleaching and aging. Image captured by Dr. Kathy Eremin.

Under the supervision of Dr. Kathy Eremin, XRF analysis was performed by the author at the Straus Center for Conservation. XRF also detected chlorine in the bleached samples. Those that were bleached and rinsed showed significantly lower levels of chlorine than papers that had been bleached without rinsing, as expected. Six Ingres drawings were also analyzed by XRF. To perform the analysis, the drawings were allowed to hang, suspended from their hinges, while their mats were supported horizontally on a table and weighted in place (Fig 12). The drawings were hung in this manner because the material of a mat board or other solid support would be analyzed along with the drawings, complicating the XRF spectra. Having air behind the drawings greatly simplified interpretation of the data. The six drawings were chosen based on their bleaching history and ability to be suspended in this manner. Two of the drawings had been

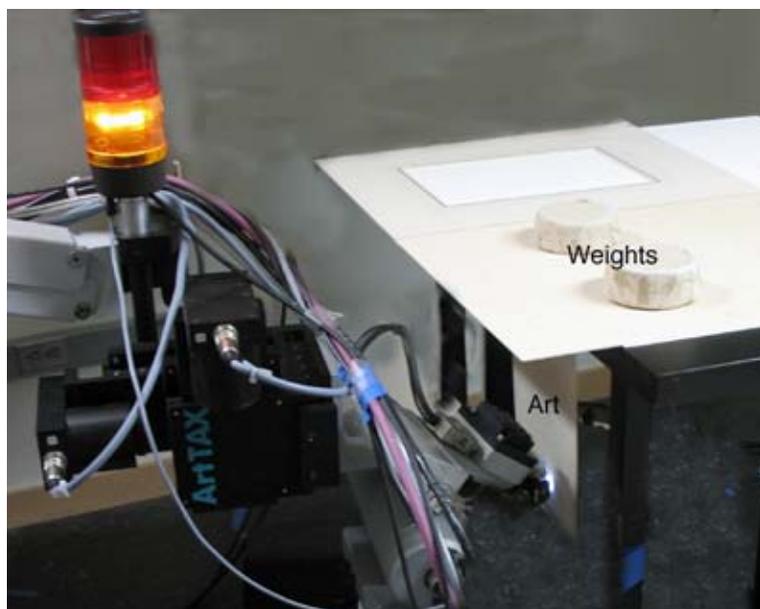


Fig. 12 Set up for XRF analysis of mounted drawings at the Straus Center for Conservation.

bleached with chlorine dioxide gas, three with Chloramine-T, and one with chlorine dioxide gas and then sodium hypochlorite. The data showed that five of the drawings had insignificant levels of chlorine, meaning that the measurements were so low, statistically speaking, they were not significantly different from zero. Only one drawing had a measurable amount of chlorine, and that was very low compared to the bleached samples (Fig. 13). This drawing was bleached with chlorine dioxide gas to treat overall foxing stains and was never rinsed.<sup>16</sup> After treatment photographs show that the bleaching treatment was successful. Today the paper has not darkened like the *Drapery Study*, but the foxing has returned. Compared to the other drawings bleached with chlorine dioxide gas, there was no difference in the method of bleaching that would explain the higher detected chlorine in this particular drawing. However, this drawing was lined, which probably made it a candidate for the gas bleaching, and the second layer of paper may have contributed to the retention of the chlorine.

Chlorine is volatile and its residues dissipate over time. If the observed darkening of the Ingres drawings was caused by chlorine residues, and not color reversion, then the damage must have occurred before the chlorine dissipated. Because chlorine wasn't detected in most of these drawings, it would seem there is a finite window of time after bleaching, during which the damage may be prevented by rinsing the residues from the paper. Experience at the Fogg Art Museum suggests that washing these drawings today may reduce some types of discoloration, but only in the short term as the color often returns.<sup>17</sup>



Fig. 13 J.-A.-D. Ingres, *Portrait of Princess Letizia Murat*, 1813, graphite on cream wove paper. Harvard University Art Museums, 1942.43. Front view in 2007. ©Straus Center for Conservation, HUAM

In conclusion to the analytical work, both SEM and XRF can detect chlorine in paper. SEM requires sampling, but can provide quantitative data and image capture, which can suggest areas for further analysis. XRF can be performed on even mounted drawings to determine if chlorine is present, but may not be useful in determining if a drawing was bleached in the past. Quoting a chemist in the Chlorite Division of Mathieson, “[t]he odor of chlorine dioxide gas may be left in the paper quite some time after the treating. This is actually residual chlorine dioxide gas. The more gas removed from a surface, the harder it gets to remove residual amounts.”<sup>17</sup> For these techniques to provide data applicable to actual artworks, many more known samples of bleached and unbleached paper must be analyzed by both methods to create libraries of comparable reference spectra. Perhaps in the future these techniques will help answer questions about the rate of chlorine dissipation from paper.

This study illustrates the challenges conservators face in trying to understand the current condition of an artwork by reconstructing past, possibly undocumented, treatments. During the late 1940s and early 1950s, many U.S. museums and collections sent drawings to the Fogg Art Museum to be treated, many were bleached. Though the literature on bleaching is voluminous,

both in the field of conservation and in the paper industry, there is still much about the bleaching of real artworks that is not understood. Further characterization of bleached historical papers would provide valuable information, not only for the Ingres drawings at the Fogg Art Museum, but for many other collections in the U.S. Analysis of all the drawings bleached with chlorine dioxide gas at the Fogg Art Museum could help clarify the long term effect of this bleach on different papers. It is hoped that this research will be expanded to Ingres drawings in other collections (especially those treated at the Fogg), looking at paper manufacture, current condition, and treatment histories. Characterizing the papers Ingres used would significantly contribute to our understanding of why drawings bleached by similar methods react differently with aging, and ultimately, allow conservators to make better-informed treatment decisions.

### **Acknowledgements**

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### **Notes**

1. This paper is part of a larger research project, *Notes Toward a History of Paper Conservation at the Fogg Art Museum, with an Evaluation of Early Bleaching Practices*,

- undertaken at the Straus Center for Conservation, Harvard University Art Museums, 2006-2007.
2. Bleaching of Paper, Rutherford John Gettens Archive, Freer Gallery of Art, Washington, D.C. Henceforth, citations for material from the Gettens Archive will be shortened to a description of the document; the folder title: FGA.
  3. RJG to Dr. Robert Feller, March 8, 1951; Feller, R.L., 1950-1958: FGA.
  4. E. F. Birkett, Jr. to RJG, February 1, 1951; Mathieson Chemical Corporation: FGA.
  5. Bleaching of Paper: FGA.
  6. *ibid.*
  7. *ibid.*
  8. *ibid.*
  9. Conservation treatment report on file in the Straus Center for Conservation, Harvard University Art Museum.
  10. Conversation with Jerry Cohn, paper conservator at the Fogg Art Museum (1960-1989), April 13, 2007.
  11. Feller, Robert. 1971. Notes on the Chemistry of Bleaching. *Bulletin of the American Group-International Institute for Conservation*. Vol. II, No. 2. 39-57.
  12. RJG to E.F. Birkett, Jr. October 29, 1951, Mathieson Chemical Corporation: FGA.
  13. Gettens, R.J. 1952. Bleaching of Stained and Discoloured Pictures on Paper with Sodium Chlorite and Chlorine Dioxide. *Museum*, Vol. V, No. 2. 116-130.
  14. Smith, T. 2005. *Reconstructing Historical Restoration Procedures for Washing and Bleaching Paper*. Thesis carried out at the Art Conservation Department, Buffalo State College, supervised by Irene Brückle and Stephanie Lussier.
  15. SEM-EDX was performed at the Museum of Fine Arts, Boston on a JEOL JSM-6460 LV Scanning Electron Microscope with an Oxford Instruments INCAx-sight EDX Spectrometer. XRF was performed on an ArtTAX Spectrometer with a Molybdenum tube, operating at 50kV and 602 $\mu$ A current, using a helium flush. The measurement diameter was about 70 microns and each measurement lasted 200 seconds.
  16. Conservation treatment report on file in the Straus Center for Conservation, Harvard University Art Museum.

17. Conversations with Craigen Bowen, paper conservator at the Straus Center for Conservation (1975-present), Fall 2006-Spring 2007.
18. E.F. Birkett, Jr. to RJG, February 1, 1951; Mathieson Chemical Corporation: FGA.

## Figures

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