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Historical Bleaching of Ingres Drawings at the Fogg Art Museum

ABSTRACT

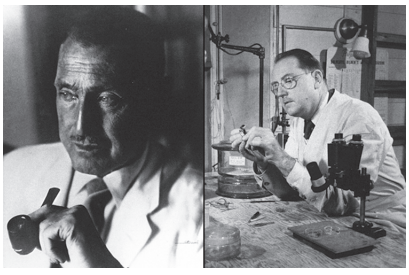
The use of chlorine dioxide gas for bleaching artworks on paper was developed by chemist Rutherford John Gettens in the Department of Conservation and Technical Studies at the Fogg Art Museum in the 1950s. After extensive testing, several Ingres drawings in graphite and black chalk were bleached by this method. To determine the cause of their current darkened condition, the drawings were examined along with their original conservation condition and treatment reports, before and after treatment photography, and Gettens's bleaching notebook. Six drawings were analyzed for chlorine residues using scanning electron microscopy and x-ray fluorescence spectroscopy.

INTRODUCTION

The Fogg Art Museum at Harvard University has the largest collection of drawings by Jean-Auguste-Dominique Ingres (1780–1867) outside of France. The drawings were created between 1804 and 1865, years that witnessed a major transformation in papermaking. The gradual adoption of machines for papermaking, the use of lower quality fibers, and the introduction of acidic sizing caused a decrease in paper quality that is recorded in Ingres' drawing papers and may have contributed to their current darkened appearance. Damage from light, poor quality mounts, and foxing have compounded the problem. 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 darkened condition and previous conservation bleaching treatments, evaluating two methods for detecting bleaching residues in paper.

BRIEF HISTORY OF CONSERVATION AT THE FOGG ART MUSEUM

In 1927 the Fogg Art Museum opened a new building under the director, Edward Waldo Forbes, and his assistant, Paul J. Sachs. Forbes and Sachs were committed not only to collecting art, but to understanding the techniques and materials of paintings and artworks. To support research in this area, Forbes created the Department of Technical Studies in 1928 with two staff members: George Stout, an art historian and conservator, and Rutherford John Gettens, a chemist (fig. 1). In the early 1930s Minna Horwitz and Evelyn Ehrlich (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



LEFT TO RIGHT

Fig. 1. George Stout, Head of Conservation (1927–1947) (left), Dr. Rutherford John Gettens, Fogg Chemist (1928–1951) (right). Courtesy President and Fellows of Harvard College

Fig. 2. Evelyn Ehrlich, Conservator (1934–1948) (left), Minna Horwitz, Conservator (1931–1949) (right). Courtesy President and Fellows of Harvard College

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transfer of Asian wall paintings. Under the supervision of George Stout and John Gettens, Evelyn Ehrlich and Minna Horwitz were responsible for paper conservation at the Museum from 1934 to 1949, when Anne Clapp began as a trainee in the department.

HISTORICAL BLEACHING AT THE FOGG

Better known for his work on the corrosion of ancient Chinese bronzes, in 1950 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" (Gettens [1950–1951]) 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, commonly known as Clorox bleach, which had been used at the Fogg Art Museum since 1937. The paper industry studied sodium chlorite for use during the bleaching of paper pulp, but unfortunately, there was no data on its effect on already formed sheets of paper.

Gettens contacted the Mathieson Chemical Corporation which donated sodium chlorite for his use, but did not have the facilities to perform the bleaching tests requested (Gettens 1951a). The chemists in Mathieson's 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" (Birkett 1951).

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 (Gettens [1950–1951]; Gettens 1951a). The first method generated chlorine dioxide gas in aqueous solution by combining sodium chlorite with formaldehyde, formic acid, or hydrochloric acid. The art work was immersed in the solution followed by rinsing, similar to the hypochlorite bleaching then in common use. Gettens found that the bleaching results were similar regardless of how the bleach was generated.

The second method involved a complex setup for making chlorine dioxide gas and running it through water to infuse the water with the gas (fig. 3). Again, the artwork would be immersed in the solution and then rinsed.

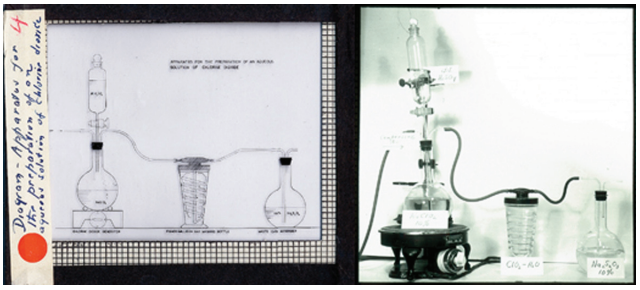

Fig. 3. Schematic drawing (left) and laboratory setup (right) for infusing water with chlorine dioxide gas. Courtesy President and Fellows of Harvard College

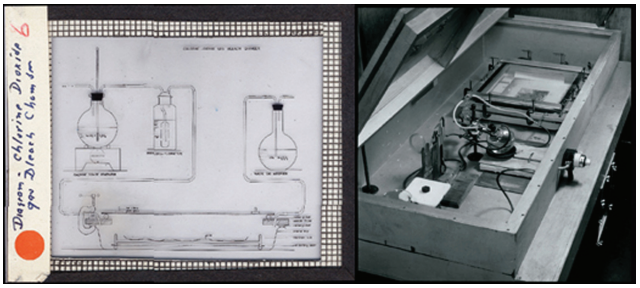

Fig. 4. Schematic drawing (left) and laboratory setup of chlorine dioxide gas bleaching chamber (right). Courtesy President and Fellows of Harvard College

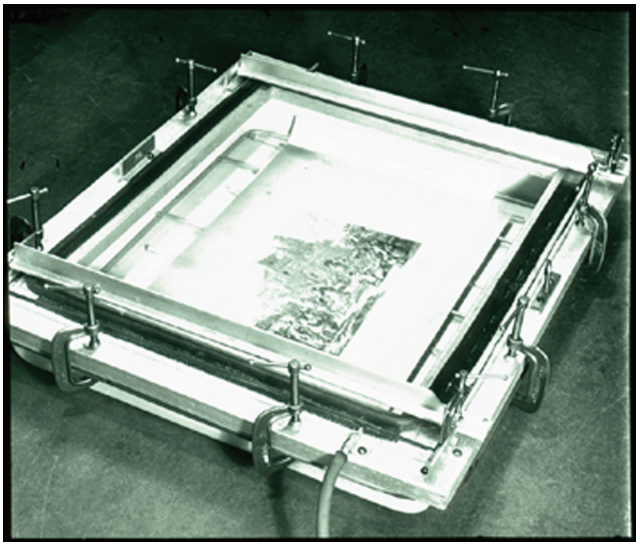

Fig. 5. Close-up view of the gas bleaching chamber with a print inside. Courtesy President and Fellows of Harvard College

The third method was only recommended when the artwork could not be immersed in bleach and rinsed afterward. The artwork would be exposed 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 after bleaching was complete. At the lower right is a close-up of the chamber with a print inside. These images are from glass slides made to illustrate Gettens's research and used for teaching in the Fine Arts Department at Harvard.

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 gas bleaching was more effective when the paper was damp or wet, vellum and casein turned a pinkish color, iron gall ink and the other inks feathered and faded, and the gas completely bleached out certain pigments, especially yellows and reds. As a result of these experiments, chlorine dioxide gas bleaching was only recommended for black-and-white prints and drawings.

Fig. 6. Pages from Gettens's bleaching notebook: chlorine dioxide bleaching tests on Windsor & Newton's Artists' Water Colours, May 7, 1951

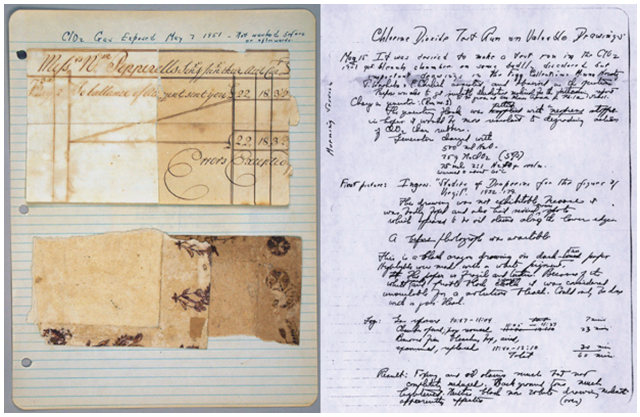

Fig. 7. Pages from Gettens's bleaching notebook: chlorine dioxide gas bleaching test on iron gall ink, May 7, 1951; chlorine dioxide gas test run on valuable drawings, May 15, 1951

Finally, Gettens began his "Chlorine Dioxide test run on valuable drawings" (Gettens [1950–1951]). These "badly discolored, but important drawings" included a drapery study by Ingres, drawings by John Ruskin, Toulouse Lautrec, Bronzino, and with the permission of the owner, a drawing on loan to the Fogg attributed to Tiepolo.

Gettens presented the preliminary results of his bleaching 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," (Gettens 1951b) but he didn't think he could return to this research. His article, "Bleaching of Stained and Discoloured Pictures on Paper with Sodium Chlorite and Chlorine Dioxide," (Gettens 1952) was published in the journal *Museum* shortly after he began working at the Freer Gallery of Art.

From research in the Fogg conservation files, it appears that chlorine dioxide gas bleaching was only used during the period of Gettens's experiments from 1950 to 1951. In all, about twenty-five prints and drawings were bleached using his three methods. Of the thirty 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 remained sodium hypochlorite, probably introduced by George Stout in the early years of the Fogg and used through the mid-1970s (Bowen 2006–2007). 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 was first mentioned in the treatment records and it was also used until the mid-1970s. Four of the drawings studied were bleached with Chloramine-T. Overall, there was no correlation between the current color of the drawings and the types of bleach that were used. In general, the papers of earlier drawings were lighter than the later drawings, which may relate to the changes in paper manufacture mentioned earlier.

EXAMINING A BLEACHED DRAWING

Utilizing the glass slides, original treatment files at the Fogg, and Gettens's bleaching notebook, about thirty Ingres drawings in pencil and black chalk treated between 1946 and 1953 were examined. Ingres' drawing, *Study for the drapery of Virgil in the Apotheosis of Homer,'* a study for a painting in the Louvre, is a good example of the complex sources of discoloration (fig. 8). On the left is the before treatment image of the drawing from 1932 and on the right the after treatment

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, 39.3 x 27.3 cm, Harvard Art Museum (1932.179); before treatment image 1932 (left), after treatment image 1951 (right). Courtesy President and Fellows of Harvard College

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, 39.3 x 27.3 cm, Harvard Art Museum (1932.179); the drawing in 2007, front view (left) and back view (right). Courtesy President and Fellows of Harvard College

image from 1951. The edges of the images are irregularly cropped by the black tape sealing the slides, which is also why they appear slightly different in proportion. In Gettens's 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" (Gettens [1950–1951]). The drawing was exposed to chlorine dioxide gas for sixty minutes after which he noted: "Foxing and oil stains much but not completely reduced. Background tone much lightened. Neither black nor white drawing material apparently affected. M. Horwitz did some additional hand work on the larger stains" (Gettens [1950–1951]).

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 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" (Gettens and Horwitz 1951a). 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, the foxing was replaced by halos of darker paper, which probably darkened from local treatment without rinsing. At the lower left and along the right edge, the paper is very mottled in tone. This is visible in the after treatment slide and was probably the result of the "additional hand work" mentioned in Gettens's 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 also visible in the 1951 slide. The back of the paper is cream, not darkened by light exposure like the front. Originally, the paper would have provided a middle tone for the black chalk and white highlights of the 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 discoloring. 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 (Cohn 2007). Though treatment documentation photos have not been found for comparison, Cohn believes the paper has not darkened again, but has maintained the tone achieved by bleaching.

BLEACHING CHEMISTRY

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 coloring matter, present. The term "chromophore" can refer 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 at the left in figure 10. 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. Each arrow represents another oxidation reaction, creating smaller and smaller molecules. If this material is not removed from the paper, over time it can reform a colored, conjugated system. It may not form the same chemical structure, however, which could be why the darkening may appear different than the original stain. This phenomenon is often generically called color reversion, though it may involve both color reversion and conversion. This problem underlies the need for rinsing after all bleaching treatments.

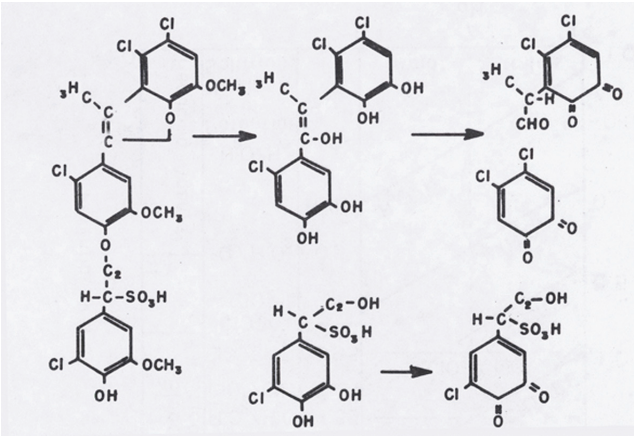

Fig. 10. Oxidation of chromophores by chlorine in aqueous solution; adapted from Robert Feller, *Bulletin of the IIC-AG* 1971

ANALYTICAL TESTING OF BLEACHED PAPERS

Another aspect of this research project was to determine if bleaching residues could be detected using analytical instrumentation. Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDX) and X-Ray Fluorescence Spectroscopy (XRF) were tested for their effectiveness in detecting chlorine in paper and their appropriateness for use on artworks. Bleached paper samples prepared for previous research (Smith 2005) at Buffalo State College were analyzed. 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 chemical mechanism as sodium hypochlorite. Samples were bleached in two ways: either brushed with 2% Chloramine-T several times without rinsing, or immersed in a 2% solution and then rinsed.

Kathy Eremin, Conservation Scientist at the Fogg Art Museum, analyzed these samples with SEM in the facilities of the Museum of Fine Arts, Boston. 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. Chlorine was successfully 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. Scanning electron microscope image of handmade, nineteenth-century, gelatin-sized, Whatman watercolor paper, after bleaching and aging; image captured by Dr. Kathy Eremin

XRF analysis was performed 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. Because of the non-destructive nature of the testing, six Ingres drawings were able to be analyzed by XRF. The drawings were hung 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 the mat board or any other solid support would be analyzed along with the drawings, complicating the XRF spectra. 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. Three of the drawings had been bleached with Chloramine-T, three with chlorine dioxide gas, and one was bleached with chlorine dioxide gas and then further bleached with

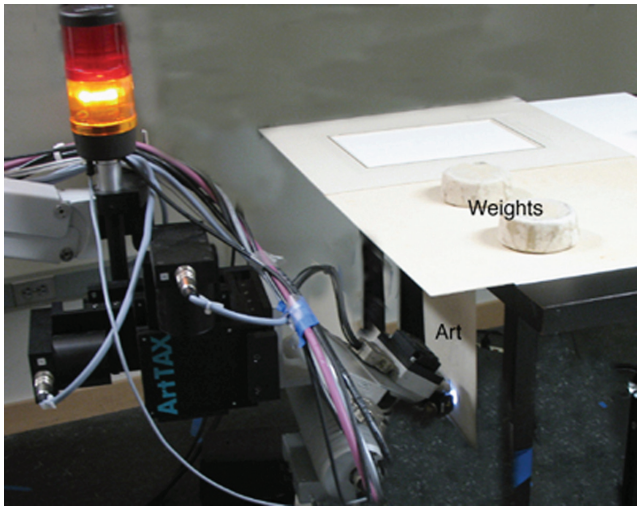

Fig. 12. Setup for XRF analysis of mounted drawings at the Straus Center for Conservation

Fig. 13. J.-A.-D. Ingres, *Portrait of Princess Letizia Murat*, 1813, graphite on cream wove paper, 26.1 x 17 cm, Harvard Art Museum (1942.43); front view in 2007. Courtesy President and Fellows of Harvard College

sodium hypochlorite. The XRF 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 (fig. 13), and it was very low compared to the bleached paper samples. This drawing was bleached to treat overall foxing stains and was never rinsed (Gettens and Horwitz 1951b). After treatment photographs show that the bleaching treatment was successful. Today the paper has not darkened, but the foxing has returned. There was no difference in the method of bleaching that would explain the higher detected chlorine in this particular drawing; however, the structure of the drawing support is different. The drawing is lined overall, which probably made it a candidate for the gas bleaching in the first place, and the second layer of paper or the layer of adhesive may have contributed to the retention of the chlorine.

Chlorine is volatile and its residues will dissipate over time. But 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" (Birkett 1951). 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. Ironically, the drawing with the most chlorine residues is not the darkest. Since chlorine wasn't detected in most of these drawings, it seems there may be a finite window of time after bleaching in which the damage occurs, and in which it might be prevented by rinsing the residues from the paper. Experience at the Fogg Art Museum suggests that washing and sun bleaching the drawings now will reduce some types of discoloration, but only in the short term as the color often returns (Bowen 2006–2007).

CONCLUSION

Both SEM and XRF can detect chlorine in paper. SEM requires sampling, but can provide quantitative data and image capture, which may suggest areas for further analysis. XRF can be performed on even mounted drawings to determine if chlorine is present, but neither method is useful in determining if a drawing was bleached in the past if the chlorine has already dissipated. New developments in hand-held XRF technology allow quantitative measurement of even very low levels of chlorine, such as were found in these artworks. For these techniques to be useful and to provide data applicable to actual artworks, many more 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 collectors sent drawings to the Fogg Art Museum to be treated and some of these 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. Analysis and comparison 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 the different papers. 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.

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, between 2006 and 2007. The project is ongoing and has been expanded to Ingres drawings in other collections, focusing on those treated at the Fogg, and looking at paper manufacture, current condition, and treatment histories. Nine drawings have been examined in the collection of the Art Institute of Chicago, one of which was bleached both at the Fogg Art Museum and at the Metropolitan Museum of Art. With the support of a fellowship from the Harvard University Library, a research trip to New York City is planned to look at Ingres drawings in the collections of the Metropolitan Museum of Art, the Pierpont Morgan Library, and the Frick Collection. In the long term it is hoped that this research will begin to identify connections between nineteenth-century paper manufacture and the outcomes of conservation treatment, allowing conservators to make better-informed treatment decisions for the works under our care.

ACKNOWLEDGEMENTS

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Craigen Bowen and the Straus Center for Conservation funded my travel during this research. Finally, I want to thank the Bryant Fellowship Committee of the Harvard University Library for funding the next stage of this project.

NOTES

1. SEM-EDX was performed at the Museum of Fine Arts, Boston, on a JEOL JSM-6460 LV Scanning Electron Microscope with an Oxford Instruments INCA x-sight EDX Spectrometer.
2. XRF was performed in the Analytical Laboratory of the Straus Center for Conservation on an ArtTAX Spectrometer with a molybdenum tube, operating at 50kV and 602μA current, using a helium flush. The measurement diameter was about 70 microns and each measurement lasted 200 seconds.

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