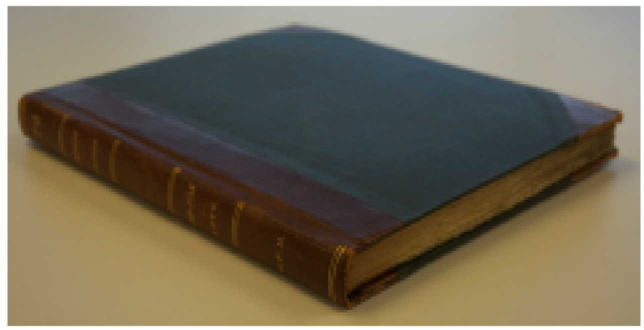
BETH ANTOINE, MARION MECKLENBURG, ROBERT J. SPEAKMAN, AND MEL WACHOWIAK

The Conservation of Letterpress Copying Books: A Study of the Baird Collection

ABSTRACT

This study investigates the conservation treatment options to preserve the treasured Smithsonian collection of letterpress copying books handwritten by Spencer Fullerton Baird (1823–1887), the second Secretary of the Smithsonian Institution. This study employs analytical techniques to investigate the complex nature of the materials, explores and evaluates treatment options with experimental procedures using artificially aged samples, and investigates best practices for the digitization of the materials. Technical analysis showed that iron II ion migration is a particularly severe problem in copying books and confirms a correlation between iron migration and the severity of ink corrosion. Several conservation treatments were conducted including anti-oxidant treatments, sizing, de-acidification, and paper splitting. One of the most promising treatments conducted is a non-aqueous anti-oxidant treatment using Tetrabutyl Ammonium Bromide [TBAB] in ethanol followed by non-aqueous de-acidification with magnesium oxide using the Bookkeeper spray and sizing with Klucel G in ethanol. Several imaging techniques were explored, and a simple and inexpensive set-up and procedure was found to give excellent results.



Figs. 1–2. Baird copying books

INTRODUCTION

Project Overview

This study investigates the conservation treatment options to preserve the treasured Smithsonian collection of letterpress copying books handwritten by Spencer Fullerton Baird (1823–1887), the second Secretary of the Smithsonian Institution. Housed in the Smithsonian Institution Archives, the Baird copying books comprise seventy-nine volumes of outgoing correspondence (1850–1877) including approximately 44,000 leaves bound in quarter-leather cloth bindings (figs. 1–2). The letters document, not only the history of the Smithsonian Institution, but also the growing fields of museology and natural history in the mid-nineteenth century. This unique primary source provides an irreplaceable window into a formative period of the history of the nation. The collection is currently unavailable to researchers due to its severely deteriorated condition as the books exhibit widespread fading and severe iron gall ink corrosion. The microfilm is largely illegible, so large portions of the information they contain are completely inaccessible.

This study employs analytical techniques to investigate the complex nature of the materials, explores and evaluates treatment options with experimental procedures using artificially aged samples, and investigates best practices for the digitization of the materials.

Presented at the Book and Paper Group Session, AIC's 39th Annual Meeting, May 31–June 3, 2011, Philadelphia, Pennsylvania.

History, Use, and Composition of Copying Books

Copying books are an early type of document copying process. They were commonly used in office environments throughout the 19th century and even as late as the 1950's (Rhodes 1999, 113). The historic copy press process involved the transfer of ink on a freshly written document to a moistened sheet of copying paper through the use of direct contact and pressure. The books were manufactured specifically for this purpose, and would have been purchased blank. The user would have written a letter on a regular sheet of writing paper but with specially formulated copying ink. A sheet of copying paper would have been dampened and the original document laid onto the damp sheet. The book would be closed and put into a copy press, transferring the ink onto the copying book page. Because the soluble copying ink was transferred directly, it left a mirror image print to be read from the verso of the thin paper (Rhodes 1999, 9).

The Conservation Challenges of Copying Books

There are several factors that make the conservation of letterpress copying books a particularly difficult problem. First of all, the volume of the materials is quite daunting. Archival collections often contain hundreds or even thousands of volumes of copying books, and a single volume contains between 300 and 800 leaves. This large quantity of materials necessitates a practical solution that can streamline the treatment and/or digitization process.

Secondly, the severity of the deterioration of copying books is distressing. In a survey conducted in 2008, 74% of questionnaire respondents reported that records in their collections were currently losing information (Antoine 2009).

Thirdly, the nature of the materials is complex and poorly understood. The unusual properties required by the copying process led to the experimentation and development of many different formulations of ink and paper (Rhodes 1999). This experimentation created not only a great variety of materials, but also a general decrease in the quality and permanence of copying inks and papers (Cleveland 2000, 24). Most copying inks are iron gall inks with additional ingredients to improve their copying capability. In order to keep the ink wet for extended periods and encourage its transfer to the copying paper, the inks and papers were impregnated with hygroscopic ingredients, such as sugar and glycerin. Colorants with high tinctorial power, such as aniline dye, were added to inks to improve the clarity of the copy and the number of copies that could be produced; and mordants, such as tannins and metal salts, were added to the papers to "fix" the ink upon contact (Cleveland and Rhodes 1999, 40). The complexity of these prepared papers and their interactions with various ink formulations are unpredictable and often disastrous. As most copying books contain many different inks that cannot be differentiated, and ink recipes vary widely, there are many variables to consider in the treatment of any single copying book.

And finally, these unusual papers and inks create special challenges for conservation treatment because they are sensitive to aqueous treatment, and they are in a bound format. The paper is vulnerable to water because the fibers were heavily beaten in order to make the paper transparent enough to read through the verso of the sheet (Rhodes 1999, 50). This technique eliminates air pockets and voids by breaking down the fiber structure and reducing porosity, making the paper appear translucent. Papers made with heavily beaten fibers are extremely hygroscopic and expand significantly when wetted, causing them to be especially vulnerable to planar distortion and dimensional changes during aqueous treatment (van der Reyden 1993, 201). The ink is quite vulnerable to cracking during aqueous treatment due to the stress caused by uneven wetting at the borders between the hydrophilic areas of the un-sized, impregnated paper and the hydrophobic areas of ink deterioration (Reissland 2000, "Side Effects," 112). The inks also become quite sticky when remoistened with water, likely due to the added humectants, which causes damage when the fragile inked areas stick to the drying support after treatment (Antoine 2009, 122). The bound format of copying books is also problematic for treatment, as disbinding dramatically changes the nature of the objects. These materials are not simply carriers of information. They are examples of an historic copying process, and their value as artifacts should be weighed in any treatment decision.

Iron Gall Ink and Copying Books: Degradation Mechanisms and Treatment Options

Iron gall ink degrades the paper substrate by two forms of decomposing reactions; namely, acid catalyzed hydrolysis and oxidation catalyzed by transition metal ions. Acid hydrolysis of cellulose is caused by the sulphuric acid inherently present in the ink. It is water-soluble and migrates out of the ink line and throughout the paper substrate with age, especially in humid or fluctuating RH conditions (Neevel and Mensch 1999, 531). Acid hydrolysis causes the depolymerisation of the cellulose molecule, resulting in the loss of mechanical strength of the substrate (Reissland and Hofenk de Graaff, 2000).

Most historic iron gall inks were made with excess iron (II) sulphate, which does not react with the tannins in the ink during ink production and remains in the material as free iron II ions. These ions are water soluble and catalyze the oxidation of cellulose through the "Fenton reaction" (Neevel and Mensch 1999, 528). This excess of iron increases with age as the tannic acid degrades causing the ratio of iron to tannin to continually increase (Krekel 1999, 56). Oxidation causes the depolymerisation and cross-linking of the cellulose, resulting in fluorescence, browning, embrittlement, and loss of mechanical strength of the substrate (Reissland and Hofenk de Graaff, 2000).

Transition metals other than iron are common in historic iron gall inks, because in addition to iron sulphate, copper and zinc sulphates were often called for in historic recipes, and many ingredients were commonly contaminated with copper, zinc, manganese, and aluminum (Krekel 1999, 55). All of these metals are destructive to cellulose and aggravate the problem of iron gall ink corrosion. Like iron II ions, copper II ions catalyze the oxidation of cellulose. Zinc sulphate can be hydrolyzed to zinc oxide, becoming a photo-catalyst for the radical oxidation of cellulose. And, aluminum sulphate and potassium aluminum sulphate (alum) can cause the acid hydrolysis of cellulose (Neevel and Mensch 1999, 531).

The severity of iron gall ink corrosion on a particular object depends not only on the composition of the ink and the object's storage conditions, but also on the depth of the penetration of the ink into the paper (Reissland 2000, "Progress," 114). Deeper penetration encourages corrosion to spread through to the verso of the substrate, causing ink drop-out or lacing. The thinness of the paper, heaviness of ink application, and amount of sizing all contribute to the depth of penetration. The hygroscopicity of copying books due to heavily beaten fibers, lack of sizing, and added humectants makes them especially vulnerable to iron gall ink corrosion by enabling the migration of soluble and destructive ink components.

Current research dictates that an appropriate treatment for iron gall ink corrosion should follow a three-pronged approach (Schafer 2004). It must arrest the acid catalyzed hydrolysis by neutralizing the sulphuric acid in the ink, deactivate or remove the transition metal ions that catalyze oxidation, and strengthen the weakened substrate mechanically when necessary. The most accepted treatment protocol currently employs an aqueous anti-oxidant treatment using calcium phytate, followed by de-acidification with calcium bi-carbonate and re-sizing with gelatin. A detailed work standard has been developed for this treatment (Huhsmann and Hahner 2008), and it has been proven unambiguously to stabilize the paper on a molecular level (Henniges and Potthast 2008, 231).

Anti-oxidants inhibit the oxidation of cellulose catalyzed by transition metal ions by interfering with the pathways of the Fenton reaction. By forming a complex with the metal ions, they eliminate coordination sites for oxidation (the Fenton reaction) to take place, thereby blocking the decomposing reaction (Neevel 2002, 76).[1]

De-acidification prevents further acid hydrolysis by neutralizing the sulphuric acid in the ink and any other acids present in the ink and paper. De-acidification has been shown to greatly improve the results of anti-oxidant treatments (Havlinova et al. 2007, 126), but treatment with a strong alkali solution is not recommended because the blue-black colorant in iron gall ink is dissolved and turns reddish-brown in pH higher than 8.0 (Krekel 1999, 57).

Gelatin has been shown to be the most effective sizing agent when re-sizing iron gall ink on paper after aqueous treatment. It seems to have the ability to fix free iron II ions present in unbalanced iron gall inks by binding them in an elastic film, thus making them inert (Kolbe 2004, 35).

Since aqueous treatment is not appropriate for the treatment of copying books, no treatment has been shown to safely chemically stabilize the rampant iron gall ink corrosion in them. Currently, the most effective treatment for copying books is mechanical stabilization by mending or lining with a solvent-set or heat-set method (Ubbink and Partridge 2003; Antoine 2009; Titus 2009).

In the last decade, a few projects have been undertaken to develop a treatment for water-sensitive objects that contain iron gall ink. These studies have built upon research into the use of halides, such as bromides and chlorides, as effective anti-oxidant alternatives to calcium phytate (Kolar et al. 2003, Kolar and Strlic 2006). Halides show great potential because they are not iron-specific, and they are soluble in organic solvents. They have the capacity to deactivate other transition metal ions, most notably copper ions, which are believed to be as destructive as iron II ions during ink corrosion (Kolar et al. 2003, 765), and they can be used in non-aqueous solution.

MATERIALS CHARACTERIZATION OF THE BAIRD BOOKS

Survey and Examination

A visual examination of each volume in the collection was conducted, seventeen samples were tested for solubility in deionized water and ethanol, and fiber analysis was conducted on twenty-one samples using a polarizing light microscope. Findings are as follows:

- There is not only a great quantity of materials, but also great variety. The papers vary in color, thickness, texture and transparency. There are an untold number of inks present with multiple inks present in all volumes. The bindings are similar in appearance, but vary slightly in construction and materials.
- Overall conditions vary from good to poor, but many volumes are very severely damaged. 89% of volumes are currently losing information. Ink corrosion is the predominant problem, as all volumes exhibit at least some symptoms (fig. 3).
- A sweet syrup smell associated with the volumes seems to correlate with severe ink corrosion (fig. 4). The source of this smell has not been identified due to time restrictions. It would be interesting to conduct Solid Phase Micro-extraction (SPME) and/or complex and simple carbohydrate spot tests to identify the material. Based on historic copying ink recipes, it is likely sugar, molasses, or honey.

Fig. 3. Example of Baird copying book in poor condition, exhibiting severe iron gall ink corrosion

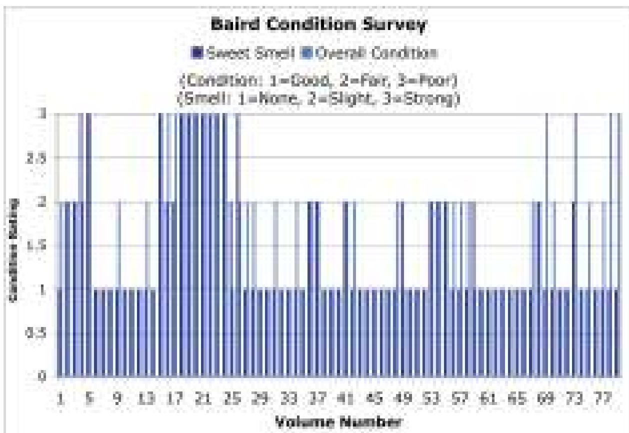


Fig. 4. Correlation between a sweet smell found in some Baird copying books and their overall condition

Fig. 5. Example of a Baird copying book in poor condition, exhibiting severe fading

- Fading is also a serious problem; 33% of the volumes exhibit severe fading (fig. 5). This problem highlights the importance of digitization and the proper storage of the materials.
- Consistent with historical research, copying papers appear to consist of fairly good quality fibers. A mix of fibers was found in all samples, most containing flax and cotton, some containing mechanical and/or chemical wood, and some possibly containing jute and/or hemp.
- Solubility testing showed surprisingly low solubility in ethanol for all inks except those containing aniline dye.
- Corroded inks cracked upon the application of water, but not ethanol.

XRF

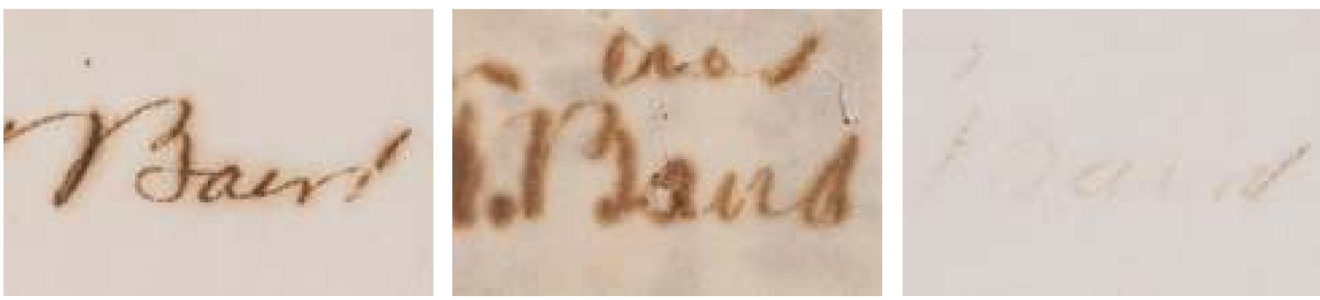
X-ray fluorescence spectrometry (XRF) was conducted to characterize the Baird materials on an elemental level using a Bruker ARTAX 800 micro-XRF spectrometer with x-y mapping capability (figs. 6–7). The XRF spectrometer identifies the elements present in a sample and can detect relative concentrations of those elements, leading to a visual representation, or area map, of the elemental components of the materials.[2] Although the sample size is too small to be definitive, results are interesting for comparison to previous theories and can help develop new ones.

Forty-one samples were selected for spot analysis. Samples were selected from fifteen volumes: five in the best condition, five with the most severe ink corrosion and, and five with the most severe fading. Each volume was analyzed in an area with ink and an area without ink for a total of thirty samples. Eleven additional samples were included to examine aniline inks, blank paper, and different inks in a single volume. Each area was analyzed at 50 kV and 600μA for a live-time count of 60 seconds. The goal of this analysis was to differentiate the components of the inks from those of the papers, to compare various inks and papers, and to determine if there is a correlation between any components and conditions.

In addition to the spot analyses, five areas of the Baird books were analyzed using the x-y mapping capability of the micro-XRF. The data from these area scans were manipulated in Microsoft Excel to create visualizations of the distribution of the elements over the samples. These area maps show differences in how the components of the inks and papers have migrated and/or interacted over time. Baird's signatures on three copied letters were analyzed: one in good condition, one severely corroded, and one severely faded. These samples were chosen to investigate the behavior of the components in materials in varying conditions. The "Dear Sir" of a severely corroded copied letter as well its corresponding original was also mapped. These samples were chosen to explore how the behavior of copying paper compares to that of a standard writing paper. To produce the XRF maps, an area was selected (ca. 8 x 30 mm) on the document and thousands of points within that area were analyzed at 50 kV and 600μA for a live-time count of 20 seconds; spacing between analyses was 0.2 mm.

The results of the spot analysis show that nearly all of the copying inks and papers in the Baird collection contain multiple transition metals in addition to iron, including copper, zinc, manganese, aluminum, chromium, and lead, illustrating


Figs. 6–7. Bruker ARTAX 800 Micro-XRF analyzing a Baird book



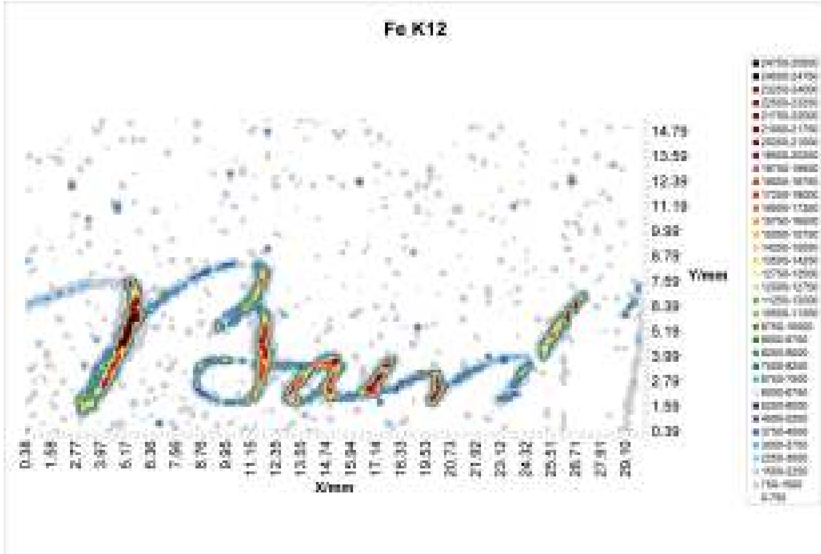
Figs. 8.a–8.o. Comparison by XRF x-y mapping of elements present in three samples of varying condition. Above left: sample in good condition; middle: sample severely corroded; right: sample severely faded. On the following four pages: 8.d–8.f iron; 8.g–8.i sulphur; 8.j–8.l potassium; 8.m–8.o calcium. Warmer colors signify higher concentration; cooler colors signify lower concentration

the need for a treatment for ink corrosion that is not iron-specific. The area maps confirm that many of the papers are impregnated with these metals, as copper, zinc, manganese, chromium, lead, tin, antimony, and aluminum were all detected throughout the paper, showing no trend with the ink line.

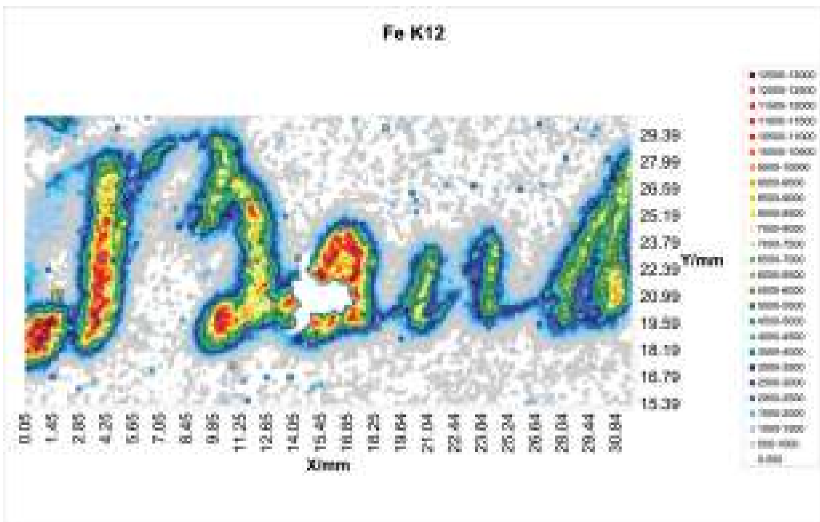
The area maps show several possible correlations between components of the materials and their conditions (figs. 8.a–8.o). The maps of iron show greater blurring of the ink lines on severely corroded samples than samples with less corrosion, indicating that there is likely a correlation between the severity of iron migration and the severity of ink corrosion. This is consistent with previous research using the iron indicator test that hypothesized that the migration of iron II ions from the ink into un-inked areas of the paper furthers the progress of ink corrosion (Eusman 2002).

It is interesting to note that the area maps show that sulphur and potassium tend to migrate more than iron, but there are no apparent correlations with condition associated with the migration of these elements. There is also a correlation between the overall quantity of iron, sulphur, and potassium present in ink and the severity of fading, as the maps show faded samples exhibit much lower quantities of these three elements than all other samples. Not surprisingly, a possible correlation was also found between the presence of calcium in the ink and the good condition of the sample, suggesting that de-acidification is likely a beneficial treatment for copying books. Calcium exhibits a strong trend with the ink in the sample in good condition, while all others exhibit only a slight trend with the ink.

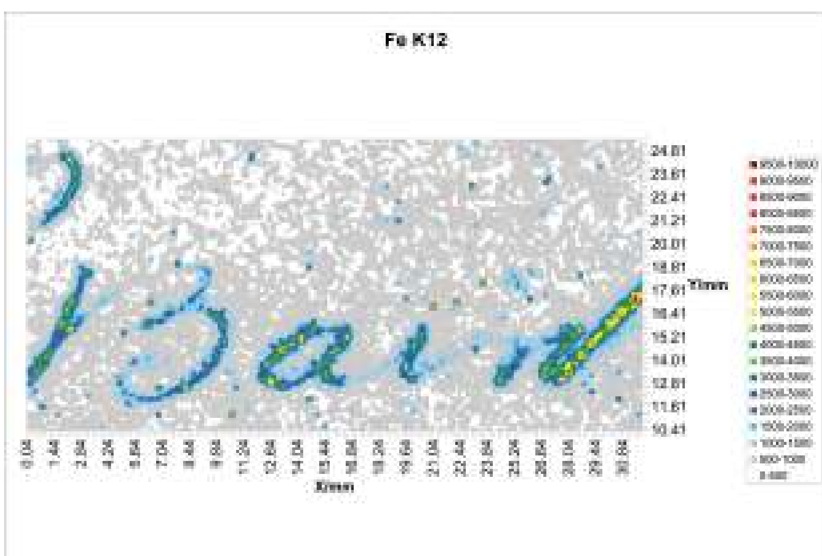
By comparing the area maps of the original letter and its copied counterpart, it is clear that the copy exhibits greater iron migration than the original (figs. 9.a–9.d). Because the inks are the same, but the papers vary, it can be speculated that the copying paper encourages iron migration. This may be due to the fact that the paper is un-sized and therefore more absorbent than the writing paper of the original. The



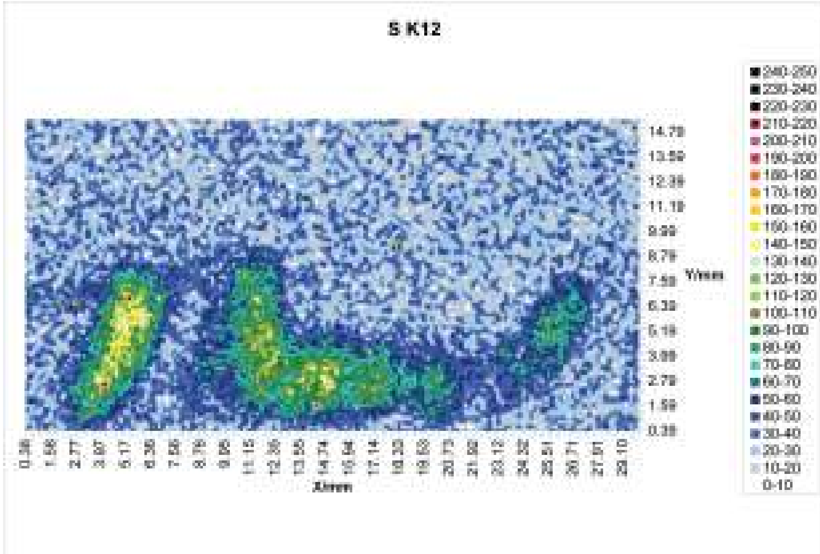
8.d



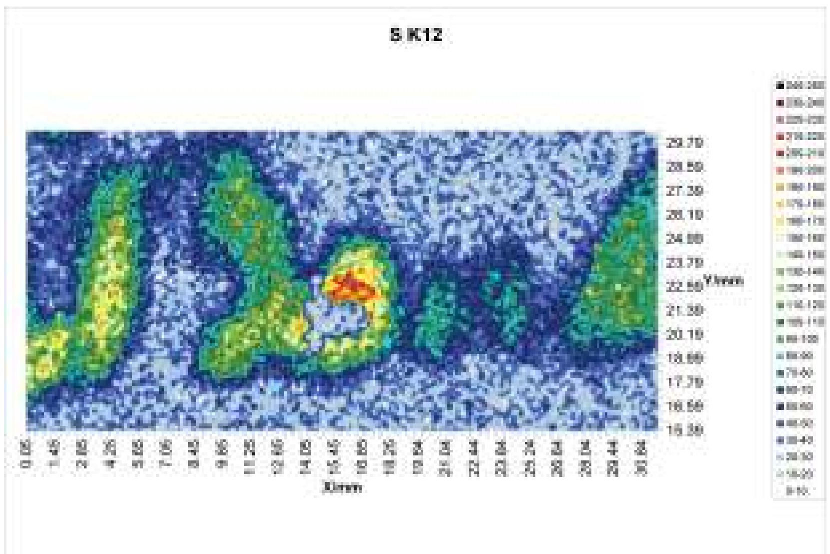
8.e



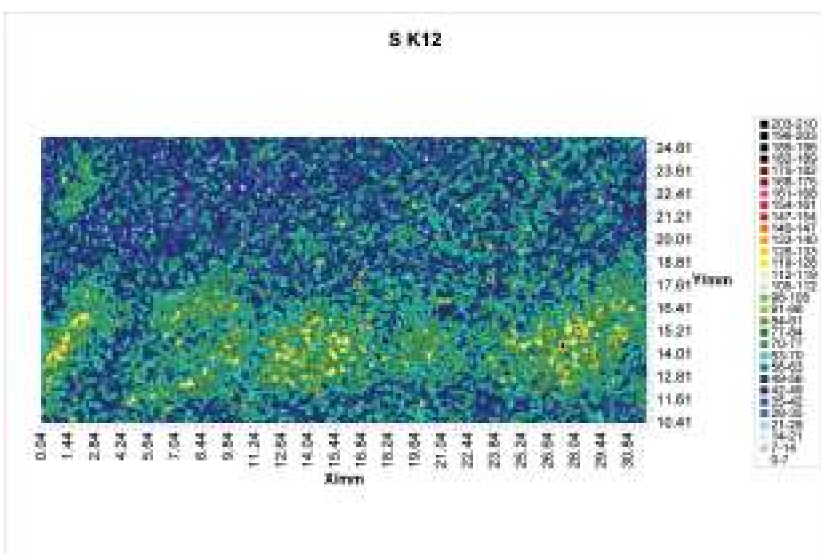
8.f



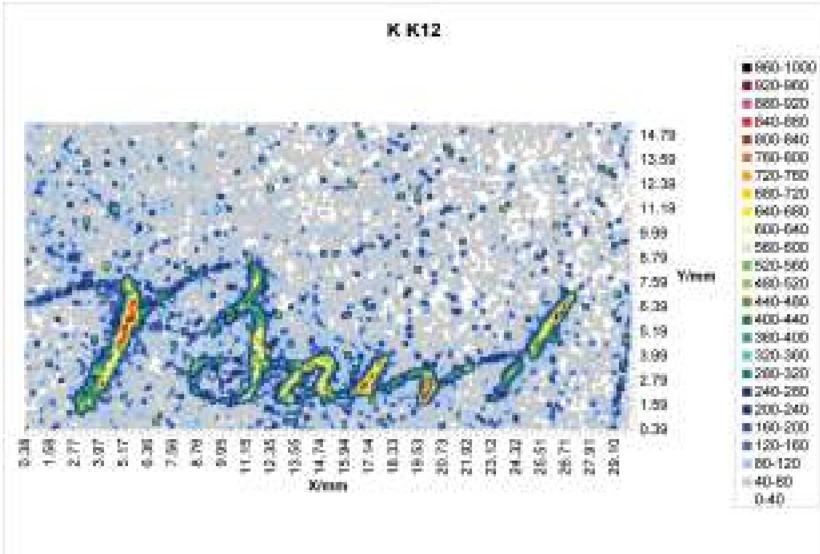
8.g



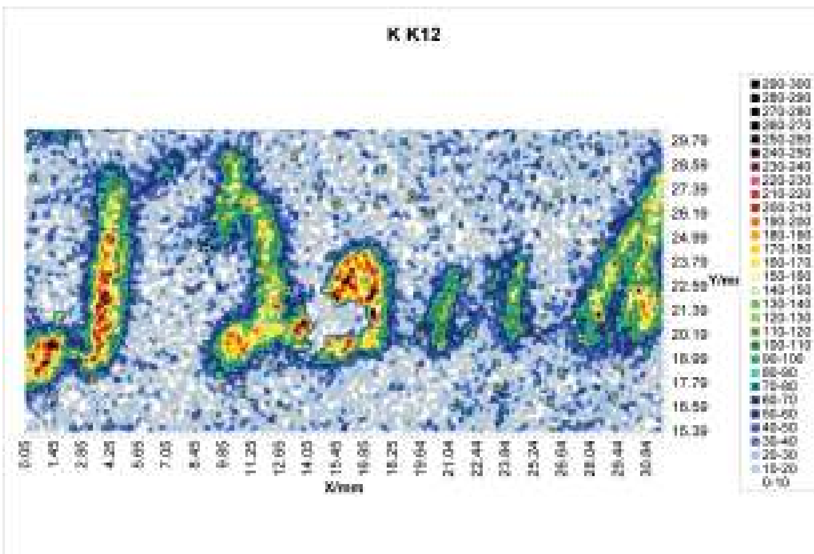
8.h



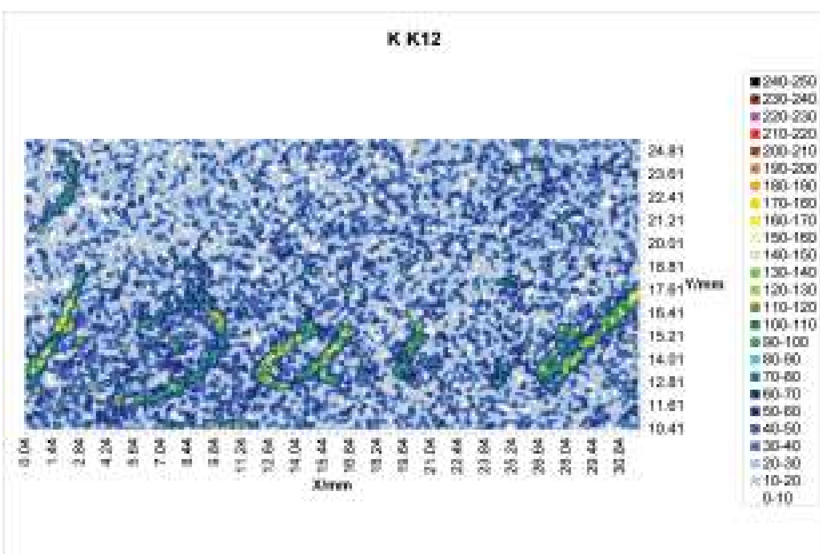
8.i



8.j

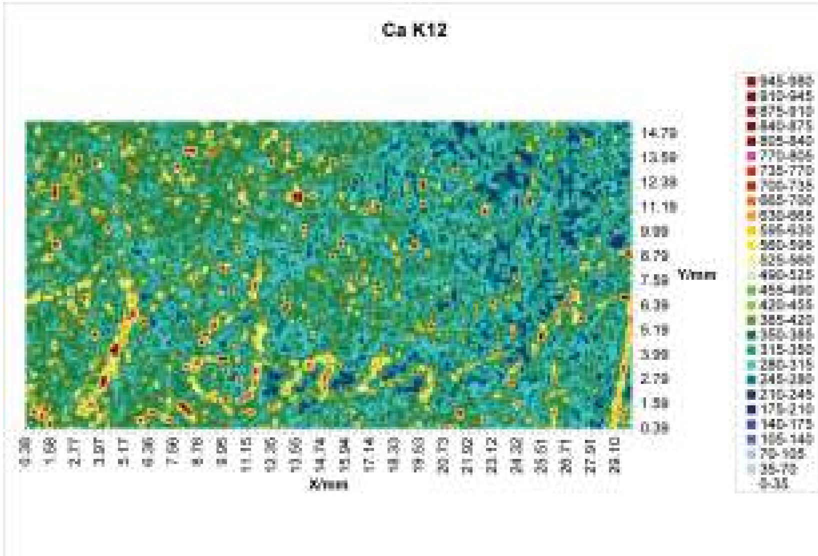


8.k

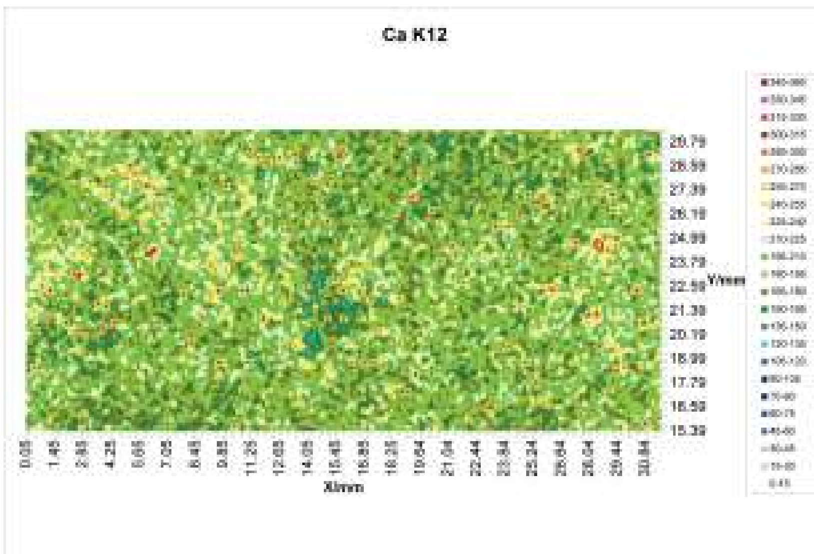


8.l

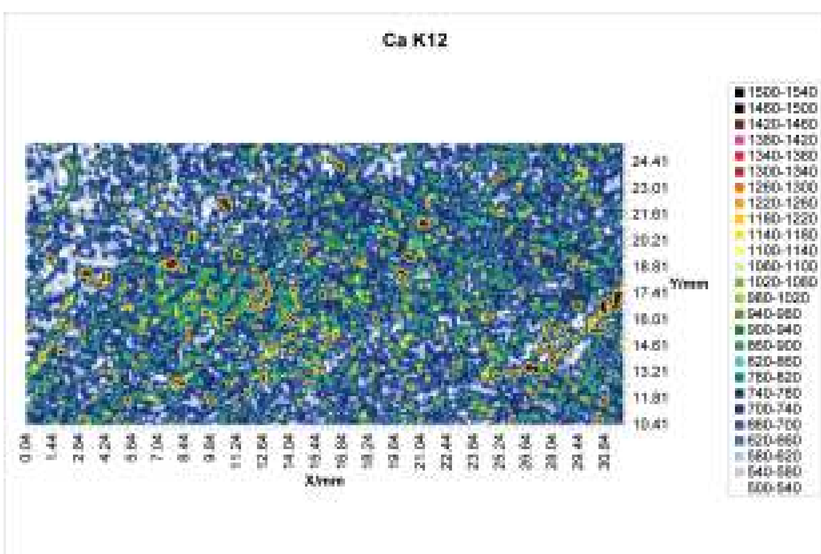
8.m

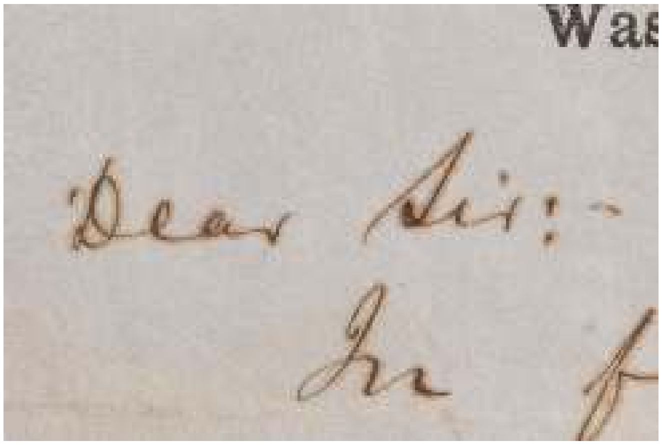


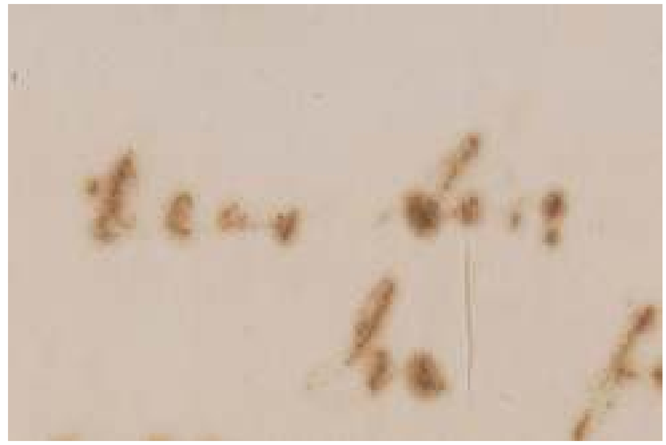
8.n



8.o

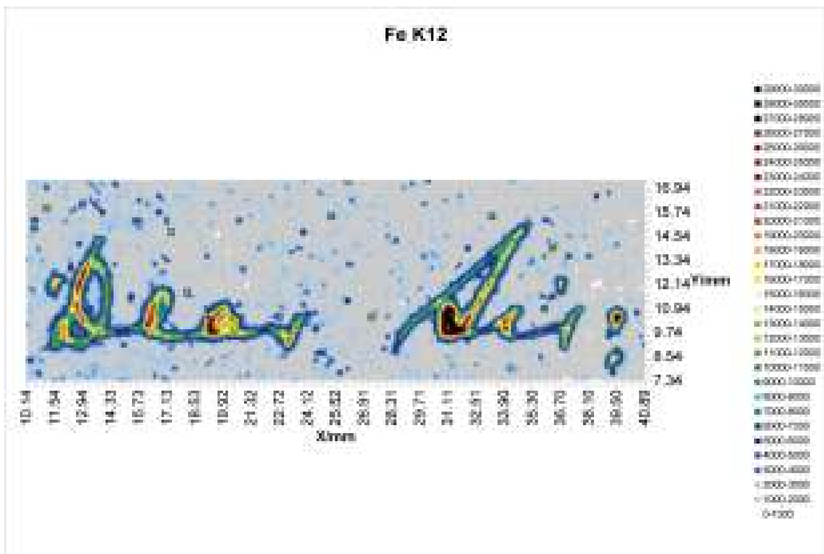




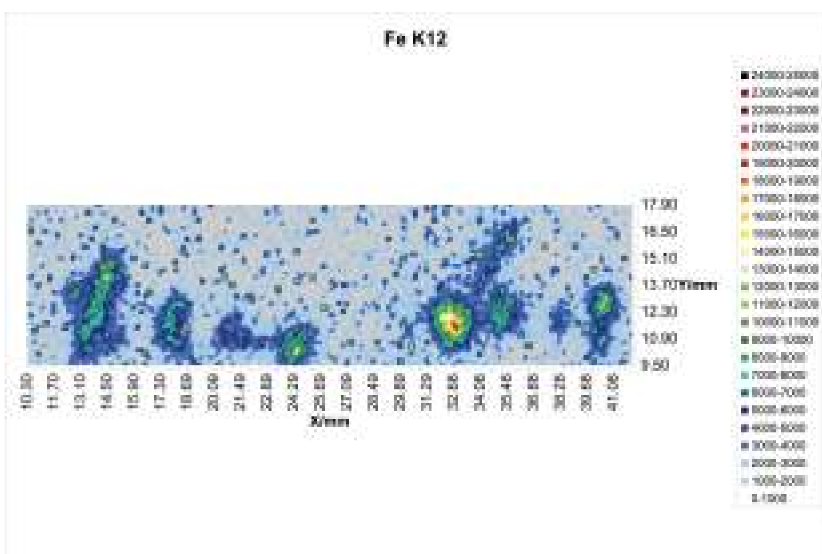


Figs. 9.a–9.d. Comparison by XRF x-y mapping of iron present in two samples, an original letter on the left and its copied counterpart on the right. Warmer colors signify higher concentration; cooler colors signify lower concentration

9.c



9.d



hygroscopic copying ink is more likely to solubilize and move into the surrounding absorbent paper in humid conditions.

TREATMENT EXPERIMENTAL

Treatment Procedures

This study experiments with the non-aqueous treatment of copying books with the anti-oxidant Tetrabutyl Ammonium Bromide (TBAB) in ethanol and its comparison to aqueous phytate treatment. TBAB is a fairly new treatment that has been researched primarily for the stabilization of copper-containing watercolor pigments, but has also been found to have a positive effect on copper-containing iron gall inks (Maitland 2009 and Malesic et al. 2005). Unlike Calcium Phytate, TBAB stabilizes iron as well as other transition metals and can be used non-aqueously in ethanol. In an effort to preserve the bindings of copying books and to streamline the process, in-situ procedures were also explored by applying the treatment solutions as a spray rather than immersion.

A total of 13 treatments were performed (fig. 10). Water and ethanol baths were included as controls. Two calcium phytate treatments were performed, both followed by de-acidification with calcium bi-carbonate, but one with and one without gelatin sizing. TBAB was applied as an immersion treatment as well as a spray at a concentration of 0.3mol/L with a dwell time of 20 minutes. TBAB was conducted alone and in combination with de-acidification with Magnesium Oxide using the Bookkeeper spray and re-sizing with Klucel G in ethanol. All spray treatments were conducted on Hollytex and blotter supports enclosed in a silicone release Mylar sandwich (figs. 11–12).

There are several concerns regarding the non-aqueous treatment of iron gall ink corrosion that must be considered (Reissland, 1999, 175). Non-aqueous treatment does not remove degradation products, iron II ions, or excess anti-oxidant. The phytate treatment relies heavily on the removal of iron II ions, and the inability to accomplish this in non-aqueous treatment is likely to reduce the effectiveness of treatment. The excess anti-oxidant is a concern because no one knows how much is used up, how much is left over, and how it reacts in the paper over time (Maitland 2010). Some treatment chemicals, such as EDTA have been found to be destructive if left in the paper (Neevel 2002, 77). Non-aqueous treatment lacks the benefit of an increase in paper flexibility due to the re-activation of fiber-to-fiber bonding (Reissland 1999, 169). And finally, the possible solubility of the inks in organic solvents is a concern. Both ethanol (TBAB in ethanol) and methanol (Bookkeeper) were used in the experimental treatments. Copying inks that include aniline dyes and deliquescent salts may be particularly vulnerable (Cleveland 2010).

Treatment #	Procedure
Treatment A	Control: No Aging / No treatment
Treatment B	Control: Aging / No treatment
Treatment C	Control: Aging / Washing
Treatment D	Control: Aging / EtOH
Treatment E	Phytate / CaB
Treatment F	Phytate / CaB / Gelatin
Treatment G	TBAB in EtOH – immerse
Treatment H	TBAB in EtOH – immerse / MgO
Treatment I	TBAB in EtOH – spray
Treatment J	TBAB in EtOH – spray / Size
~~Treatment K~~	~~TBAB in EtOH – suction table~~
Treatment L	TBAB in EtOH – capillary washing
Treatment M	TBAB in EtOH – spray / MgO / Size
Treatment N	TBAB in EtOH – spray / MgO / Size / Line
~~Treatment O~~	~~Non-aqueous Paper Splitting~~

Fig. 10. Experimental treatments performed

Fig. 11. Experimental treatments in progress: phytate immersion treatments

Fig. 12. Experimental treatments in progress: TBAB spray procedure

Sample Preparation

Sample copying papers were prepared for the treatment experimental by applying copying inks made in the lab to blank copying pages cut from two volumes of the Baird books, in addition to a known modern Gampi tissue paper with properties similar to copying paper (figs. 13–14). For the purposes of this experiment, copying ink was defined as a writing ink that includes an additional hygroscopic ingredient, such as sugar or glycerin. The iron gall ink recipe used for research at the Library of Congress (LC) was used as a control. Several variants of copying inks were made by adding ingredients to this control ink. Additional components included sugar, glycerin, deliquescent salt, copper sulphate, alum, potassium chromate, Prussian blue, aniline dye, and logwood dye. Two complex inks from historic recipes were also used in order to more accurately mimic an ink and paper combination that would be found in collections materials. A total of eight inks were applied in two lines of varying width using a Pilot Parallel Pen, which gives a constant line thickness no matter at what angle the pen is held. The main components of the sample inks are listed below. The samples were aged in an aging oven at 70 degrees Celsius and 50% RH for four days prior to treatment and for an additional nine days in the same conditions after treatment.

Fig. 13. Sample preparation: ink ingredients

Fig. 14. Sample preparation: sample inks

Sample inks:
1. Control: LC iron gall ink
2. LC iron gall ink plus sugar
3. LC iron gall ink plus glycerine
4. LC iron gall ink plus sugar and Prussian blue
5. LC iron gall ink plus glycerine and aniline dye
6. Complex historic iron gall copying ink with copper
7. LC iron gall ink plus deliquescent salt
8. Historic logwood bi-chromate ink with ferrous sulphate but no gall nuts

Treatment Evaluation

Evaluation of treatment effectiveness and side-effects were considered for archival materials, not works of art. These materials are valued primarily for the information they contain, so the importance of legibility and stability is paramount, while minor color shifts and other visual changes may be tolerated.

The samples were tested for strength, pH, and iron migration before and after treatment, and the treatments were evaluated for solubility problems, color changes, risk of treatment, practicality, and health and safety concerns.

All eight inks were monitored for iron II ion migration with an iron indicator test before and after treatments and again after post-treatment aging. The indicator paper is filter paper impregnated with bathophenanthroline, which reacts with iron II ions to form a pink complex (figs. 15–16). The paper was dampened and lightly pressed to the samples for 30 seconds, creating a pink stain where it was in contact with iron II ions. It is not a quantitative test, but relative concentrations can be determined by comparing the darkness of the stain, as long as variables such as surface sizing and length of exposure are controlled. This test illustrates the effects of aging and treatment on the movement and relative quantity of iron II ions in a sample.

Cold extraction pH testing was performed for treatments on all three sample papers according to ASTM designation: D778-97 (re-approved 2002). Results are shown in figures 17, 18, and 19. Because sample material was limited, 0.1g of paper was tested in 7.0 ml of distilled water in keeping with the ratio from the standard.

Samples were tested for tensile strength before treatment and after post-treatment aging. Using tensiometers in climate-controlled cases, samples were subjected to increasing tension until their breaking point (figs. 20–21).

Fig. 15. Iron II migration testing

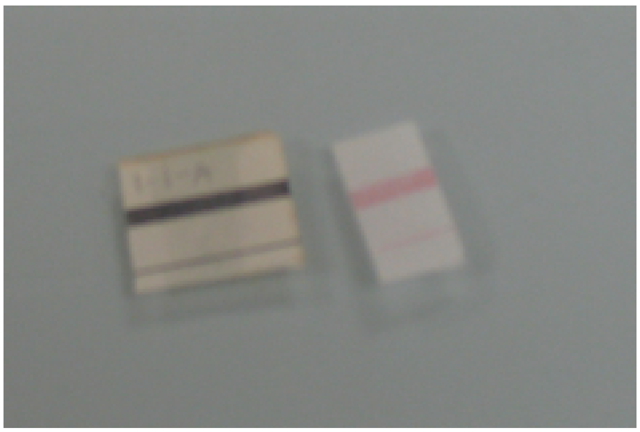


Fig. 16. Iron II migration testing

Summary and Discussion of Findings

- As expected, aqueous treatments were effective at removing iron II ions, increasing pH, and restoring strength to the samples. The effectiveness of the TBAB treatments varied, but none were as effective as the aqueous treatments.
- Treatment with gelatin significantly improved the strength and pH of the samples.
- Although comparison with the ethanol control treatment shows that TBAB treatments do have a positive effect beyond the ethanol, TBAB alone did not cause significant improvement in the properties of the samples.
- It is possible that left over TBAB in the paper after treatment causes a detrimental effect that is counteracting the positive effect of the de-activation of the transition metal ions. There was concern for this problem before the project began because non-aqueous treatment does not rinse out excess treatment solution.
- MgO and Klucel G together significantly improve the performance of TBAB. Treatments combining these elements are not as effective as the phytate treatment, but they may be useful for non-aqueous applications.

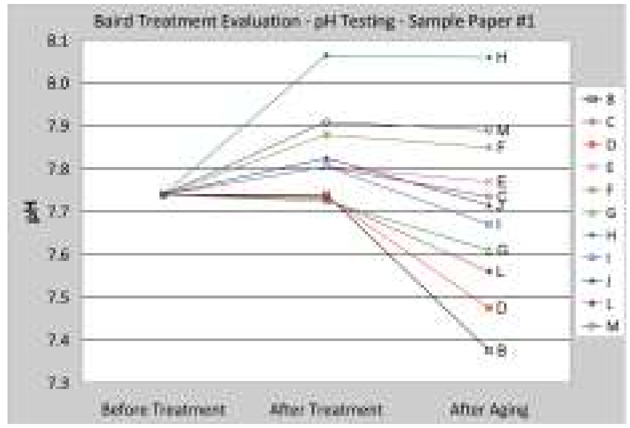


Fig. 17. Results of pH testing: Sample paper #1 before treatment, after all treatments, and after post-treatment aging

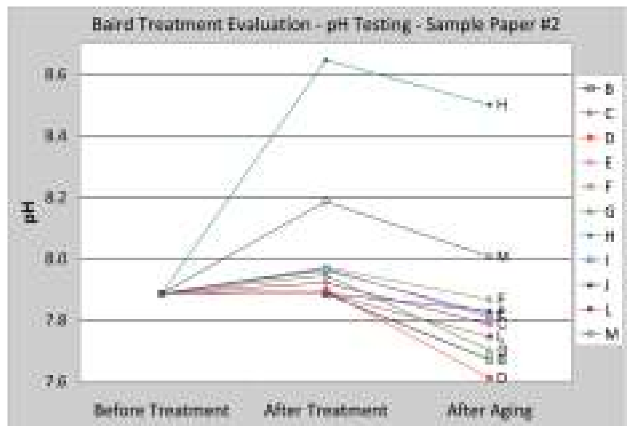


Fig. 18. Results of pH testing: Sample paper #2 before treatment, after all treatments, and after post-treatment aging

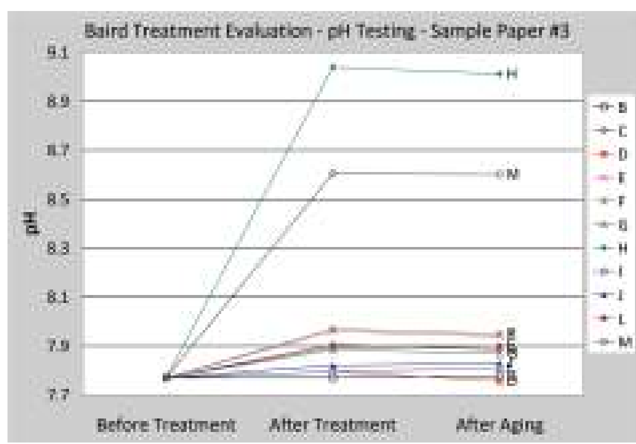
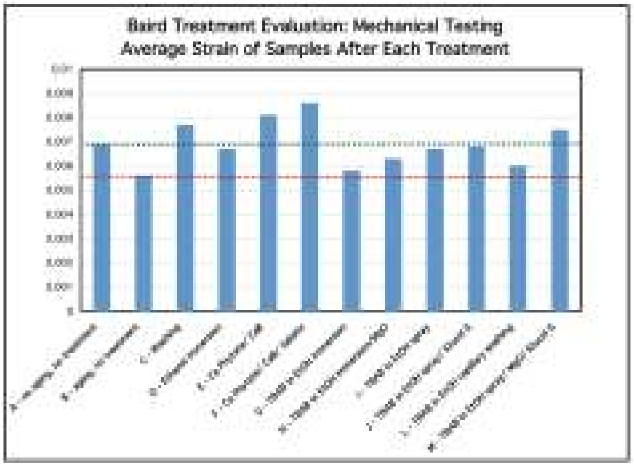
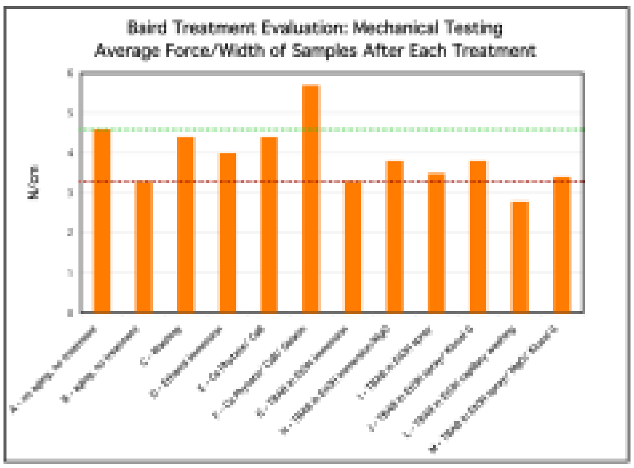


Fig. 19. Results of pH testing: Sample paper #3 before treatment, after all treatments, and after post-treatment aging





Figs. 20–21. Results of mechanical testing. Average strain and average force/width of paper samples after each treatment after discarding outliers and errors. The horizontal lines represent the control groups A and B. Results are interpreted as follows: (1) An increase in strain (elongation) and an increase in force at breaking indicates an overall improvement in the properties of the samples when compared to the control groups, Treatments A or B, (2) A loss of strain and a loss of force indicate ineffective reinforcement of the samples when compared to group A or a detrimental effect when compared to group B, and (3) An increase in strain and a loss of force indicates an increase in flexibility

- Although both types of sizing improved the performance of treatment, they also caused the papers to become stickier and may cause problems when drying. Adjusting the treatment procedure by spraying the verso only and drying by laying the object recto side up on silicone-release Mylar and covering with Hollytex and blotter or felt, may reduce or eliminate the problem.
- Solubility is a concern for both aqueous and non-aqueous treatment, so thorough testing should be an important component of any treatment protocol. Based on observation during treatment, it appeared that the only ink that had severe solubility problems in ethanol was the one containing aniline dye. Most others fared quite well. The spray procedure reduced solubility problems, especially when sprayed from the back. Although solubility remains a concern for treatment with ethanol, even the most severe fading was very minor and would likely not have caused illegibility unless the text was extremely faint before treatment. It is also interesting to note that the only ink that did not exhibit any solubility problems was the control ink, the only ink in the study that is not a copying ink.
- The spray procedure has several benefits. It allows in situ treatment to avoid disbinding; it increases the safety of treatment by allowing the controlled application of solutions to only one side of the object; and it is fast, efficient, and requires less exposure to chemicals than immersion treatment.
- MgO should be used cautiously, as it can increase the pH beyond the recommended limit of 8.0 for alkaline-sensitive iron gall ink.
- Sample ink #6, a complex ink made from an historic recipe performed the worst in iron migration testing for all treatments and was significantly weaker than all other samples, before and after all treatments. As expected, the LC ink recipe creates a relatively stable iron gall ink, while complex, historic inks are more likely to be unstable.
- During the post-treatment aging of the samples, it became clear that the inks that contain sugar developed much darker and larger brown halos around them than the others (figs. 22–23). This could indicate that the most severe deterioration in copying books is caused by the inclusion of sugar in the inks and/or papers. This observation is consistent with the correlation between poor condition and the sweet smell noted during the survey. All aqueous treatments completely removed this discoloration. TBAB alone was less effective at removing it, but in combination with Klucel G and MgO, it was slightly more effective. Ultraviolet examination of florescent haloing is consistent with visual examination of the brown haloing.
- The samples become much flatter and less cockled after aqueous treatments than ethanol treatments. While flatter is usually more desirable in paper conservation, the cockled samples actually appear more similar to collections materials after treatment, because copying papers were distorted when originally copied, due to the damp copying process.
- Paper-splitting is not a practical or safe option for the treatment of copying books. The thinness of the paper and its sensitivity to moisture make paper splitting risky. Paper-splitting is more commonly used for printed materials like brittle newspapers, which are not unique. If the damage is caused to copying book material by the splitting process, replacement is not possible. The process is also too time-consuming to be considered a viable option unless it can be done by a mechanized process. Currently, this service is not offered commercially anywhere internationally.

Figs. 22–23. Samples before aging, top, and after post-treatment aging, showing brown haloing around inks containing sugar, bottom

IMAGING AND DIGITIZATION EXPLORATION

Copying books present quite a few challenges for digitization, stemming from the translucence of the paper, the bound format, faint and feathered ink, the fragile substrate, cockling and creasing, and the overwhelmingly large volume of material. With the goal of developing a protocol to gain excellent results using inexpensive and accessible equipment, several imaging techniques were explored and a simple and practical set-up and procedure was found.

Experimentation was conducted using a Canon 5D Mark II digital camera on a copystand with a Canon 100mm macro 2.8 lens, a Canon 50mm 1.4 lens, two Canon Speedlite 580 EX with diffusers, a Micro RingLite MR-14EX, and two Tiger UV lights.

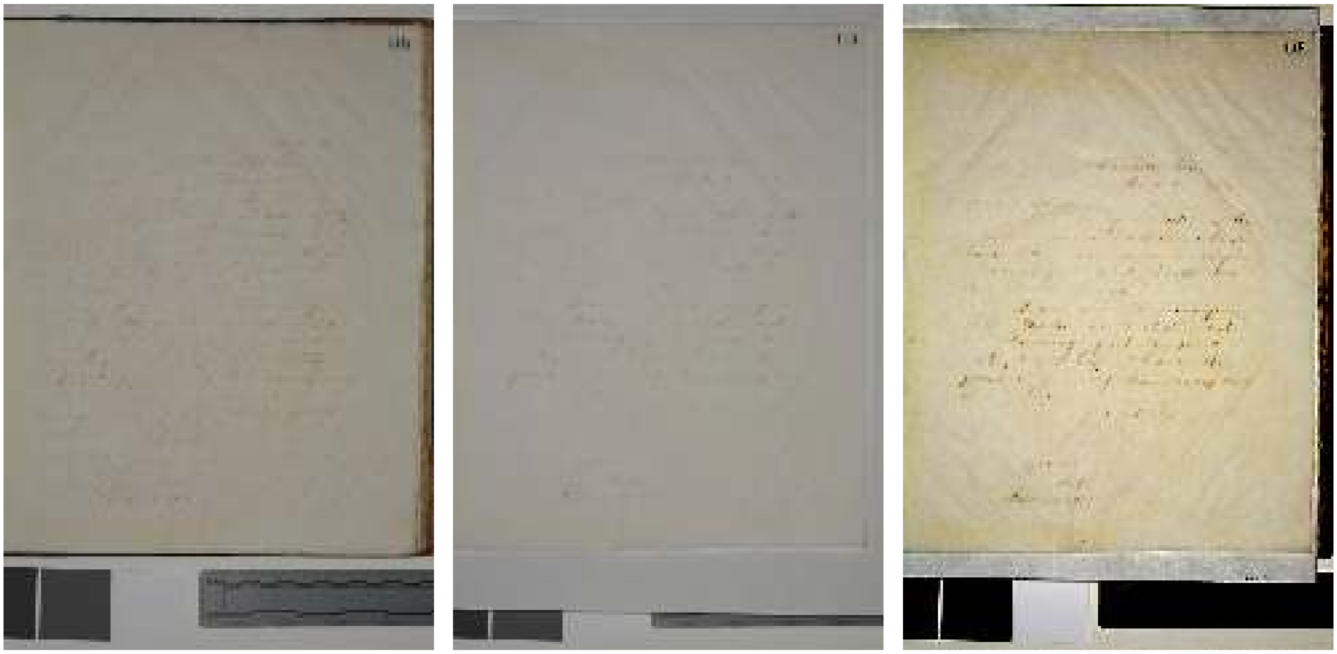
Most light sources provided unsatisfactory images as they intensified the distracting elements of the materials. Transmitted light highlighted discoloration from water staining and ink offset, while traditional reflected light set-ups enhanced distracting shadows from surface texture and cockling. For non-faded text, ultraviolet (UV) light caused the writing to appear darker and blotchier, which reduced legibility.

The best results were achieved by placing the book on a copy stand on a book cradle that allowed one side to remain flat while elevating the facing side. An interleaving sheet of Phototex paper was placed directly under the leaf to be imaged in order to counteract the translucence of the sheet. Phototex was chosen because it contains no optical brighteners that would fluoresce under UV light and because it is very soft and safe to use with the fragile paper. Many archival papers would be appropriate to use, but distracting watermarks and optical brighteners should be avoided. A ring flash was attached to the lens of a digital camera. A ring flash is literally a ring of light that provides a very even light and projects directly down onto the object at a perpendicular angle. This light source eliminates the distraction in the image from surface textures and cockling (figs. 24–26). For faint text, UV light was used instead of the ring flash. Most of the faint iron gall ink that is virtually invisible in normal light became legible under UV (figs. 27–28). Simple image processing techniques such as compressing the histogram to enhance the brightness and contrast and un-sharp masking improved most of the images dramatically. By converting the images from RGB to CIELab color space (This can be done in Photoshop by selecting the Image menu and changing the Mode to "Lab color.") and working only with the lightness, all of the information is retained, but the image is cleaner without the distraction of color. The contrast and brightness was increased using the Curves function by adjusting the mid-tones only, leaving the lightest lights and the darkest darks alone. Blurred and feathered text proved to be the most challenging problem, and only limited success was achieved (figs. 29–30).

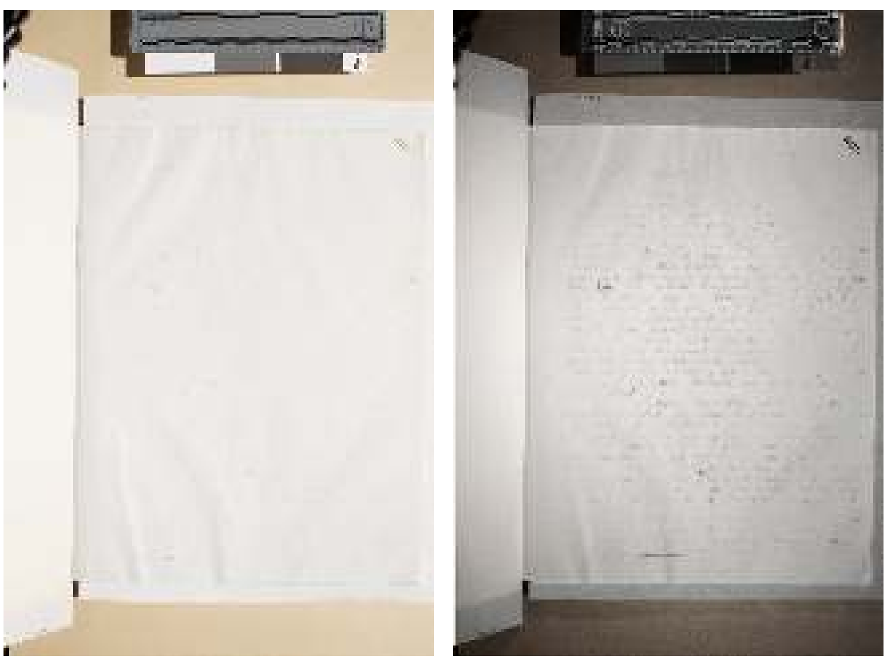
CONCLUSIONS

The complex composition of copying book papers and inks complicate the problem of iron gall ink corrosion by enabling the rapid migration of sulfuric acid and transition metal ions. The large quantity of materials and their moisture sensitivity limit conservation treatment options to moderately effective non-aqueous anti-oxidant treatments or mechanical stabilization. Considering the complexity and fragility of the materials and the difficulties of conservation, digitization and proper storage should be very high priorities in any preservation plan concerning copying books.

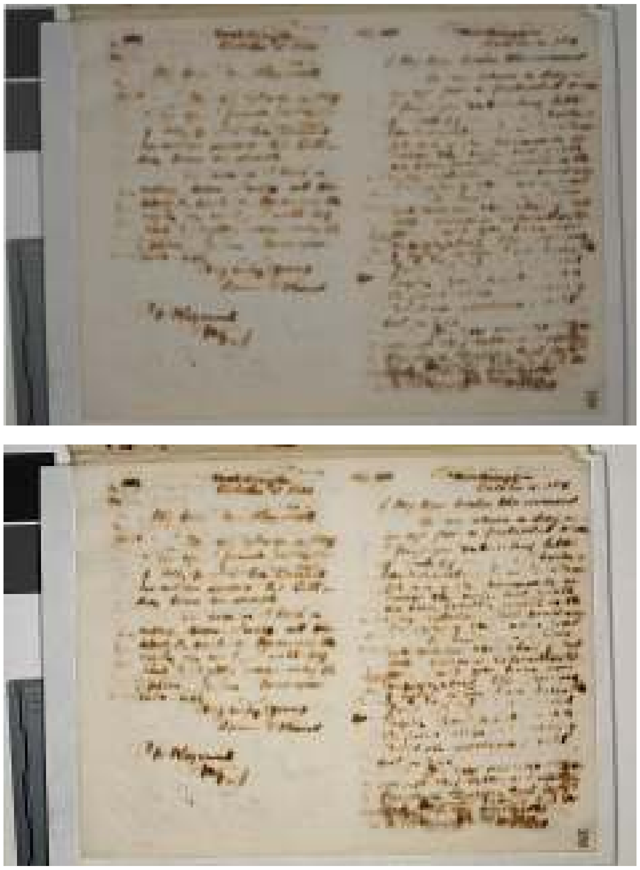
Although the TBAB treatments were found to be less effective at reinforcing the samples as the aqueous phytate treatments, especially the one with gelatin, most do show some improvement over the untreated, aged samples. All forms of evaluation agree that the best TBAB treatment is Treatment M, the spray procedure with MgO and Klucel G, and that the TBAB treatment needs the help of de-acidification and resizing to have a significantly positive effect. The possibility that the leftover TBAB in the paper has a



Figs. 24–26. Baird copying book, volume 71, page 118. Example of Baird copying book digitization using interleaving, a ring flash, and image processing to increase legibility and decrease distraction from translucency, distortion, and surface details. Left, page photographed in reflected light with a ring flash and no interleaving and no image processing. Middle, page photographed in reflected light using a ring flash with an interleaving sheet and no image processing. Right, page photographed in reflected light using a ring flash with an interleaving sheet and minimal image processing using Digital Photo Professional



Figs. 27–28. Baird copying book, volume 9, page 208. Example of Baird copying book digitization using UV light and image processing to enhance faint text. Left, page imaged in normal light with no image processing. Right, page imaged in UV light with minimal processing using Digital Photo Professional, manufactured by Canon



Figs. 29–30. Baird copying book volume 15, page 138. Example of Baird copying book digitization using image processing to increase the legibility of blurred and feathered text

detrimental effect is cause for concern, but the inclusion of MgO and Klucel G seems to mitigate any negative effect.

Experimentation with in situ procedures was fruitful, as the spray procedure was found to have several benefits. It allows in situ treatment to avoid disbinding; it increases the safety of treatment by allowing the controlled application of solutions to one side of the object; and it is fast, efficient, and requires less exposure to chemicals than immersion treatment.

Overall, the experimentation of non-aqueous treatment with TBAB led to a step in the right direction, but not a solution to the problem of the conservation of letterpress copying books. As often occurs in research, it also raises many more questions. The clear benefits of aqueous treatment and gelatin pique interest in the testing of anti-oxidant solutions with gelatin in various mixtures of ethanol and water. Perhaps an 80:20 ethanol/water solution would provide the benefits of aqueous treatment while avoiding its problems. Additionally, during the course of this study, two alkylimidazolium bromides have been shown to be more effective than TBAB for the non-aqueous treatment of ink corrosion, 1-ethyl-3-methylimidazolium bromide [EMIMBr] and 1-butyl-2,3-dimethyl-imidazolium bromide [BDMIMBr] (Kolar et al. 2008). It would be very useful to test these anti-oxidants combined with de-acidification and sizing on copying book samples.

NOTES

1. Kolar et al. 2005 includes a detailed description of the three types of anti-oxidants: peroxide decomposers, chelating agents, and radical scavengers; and the mechanisms employed by each of them.
2. XRF spectrometry is among the most widely used and versatile of all instrumental analytical techniques. An XRF spectrometer uses primary radiation from an X-ray tube to excite secondary emission from a sample. The radiation emerging from the sample includes the characteristic X-ray peaks of elements present in the sample. Dispersion of these secondary X-rays into a spectrum permits identification of the elements present. The height of each characteristic X-ray peak relates to the concentration of the corresponding element in the sample, allowing quantitative analysis of samples for many elements in the concentration range from low parts-per-million to 100%. XRF spectrometers can simultaneously measure elements that occur in the range from Na (11) to U (92). Depending on the sample matrix, XRF generally produces compositional data for approximately 15 major and minor elements with good precision and accuracy and is 100% nondestructive. The instrument used for this study is equipped with a molybdenum target polycapillary lens X-ray tube that has ca. 80 μm spatial resolution. The X-ray detector is a Si drift detector with a 10 mm^2 active area and energy resolution of ca. 143eV for the Mn Ka at 100kcps.

REFERENCES

Antoine, Beth. 2009. "Letterpress Copying Books: Conservation and Preservation Implications." The Book and Paper Group Annual 28: 121–124.

Banik, Gerhard. 1997 "Decay Caused by Iron-gall Inks." Proceedings of the Iron Gall Ink Corrosion Symposium, Museum Boijmans Van Beuningen, Rotterdam, April 1997. Amsterdam: Netherlands Institute for Cultural Heritage. 21–26.

Cleveland, Rachel-Ray. 2000 "Selected 18th, 19th and 20th Century Iron Gall Ink Formulations Developed in England, France, Germany, and the United States, for use with the Copy Press Process." Postprints of the The Iron Gall Ink Meeting, Newcastle Upon Tyne, England: University of Northumbria, 23–30.

Cleveland, Rachel-Ray. 2010 Personal Communication.

Eusman, Elmer. 2002 "Effects of Aqueous Treatment on Iron Gall Ink—Monitoring Iron Migration with the Iron (II) Indicator Test." In The Broad Spectrum: Studies in the Materials, Techniques, and Conservation of Color on Paper, ed. Harriet K. Stratis and Britt Salvesen. 122127. London: Archetype.

Eusman, Elmer and Cyntia Karnes. The Ink Corrosion Website. European Commission of Preservation and Access in Amsterdam, Museum Boijmans van Beuningen in Rotterdam, Netherlands Institute of Cultural Heritage in Amsterdam, the National Archief in The Hague, and the Teyler Museum in Harlem. http://www.knaw.nl/ecpa/ink/index.html (accessed Nov 10, 2010).

Havlinova, Bohuslava, et al. 2007. "The Conservation of Historical Documents Carrying Iron-gall Ink by Antioxidants." Restaurator 28 (2): 112–128.

Henniges, Ute and Antje Potthast. 2008. "Phytate Treatment of Metallo-gallate inks: Investigation of its Effectiveness on Model and Historic Paper Samples." Restaurator 29: 219–234.

Huhsmann, Enke and Ulrike Hahner. 2008. "Work Standard for the Treatment of 18th and 19th Century Iron Gall Ink Documents with Calcium Phytate and Calcium Hydrogen Carbonate." Restaurator 29: 274–319.

Kolar, Jana, et al. 2003. "Stabilization of Corrosive Iron Gall Inks." Acta Chim. Slov. 50: 763–770.

Kolar, Jana, Jasna Malasic, and Matija Strlic. 2005. "Anti-oxidants for the Stabilization of Iron Gall Ink Corrosion." 14th Triennial Meeting, The Hague, 12–16 September 2005: Preprints (ICOM Committee for Conservation), ed. Isabell Verger. N.p.: James & James, 186–192.

Kolar, Jana and Matija Strlic, eds. 2006 Iron Gall Inks: On Manufacture, Characterization, Degradation, and Stabilization. Ljubljana, Slovenia: National and University Library.

Kolar, Jana, et al. 2008. "New Anti-oxidants for Treatment of Transition Metal Containing Inks and Pigments." Restaurator 29 (3): 184–198.

Kolbe, Gesa. 2004. "Gelatin in Historical Paper Production as an Inhibiting Agent for Iron Gall Ink Corrosion on Paper." Restaurator 25 (1): 26–39.

Krekel, Christoph. 1999 "The Chemistry of Historic Iron Gall Inks." International Journal of Forensic Document Examiners. 5 (Jan/Dec): 54–58.

Maitland, Crystal. 2009. "Where Archival and Fine Art Conservation Meet: Applying Iron Gall Ink Antioxidant and Deacidification Treatments to Corrosive Copper Watercolors." The Book and Paper Group Annual 28: 37–46.

Maitland, Crystal. 2010 Personal communication.

Malesic, J., J. Kolar, M. Struc and S. Polanc. 2005. "The Use of Halides for Stabilization of Iron Gall Ink Containing Paper – The Pronounced Effect of Cation." e-Preservation Science 2: 13–18. www.e-PreservationScience.org

Neevel, Johan G. and Cornelis T.J. Mensch. 1999. "The Behavior of Iron and Sulphuric Acid During Iron Gall Ink Corrosion." 12th Triennial Meeting, Lyon, 29 August-3 September 1999: Preprints (ICOM Committee for Conservation) N.p.: James & James, 528–533.

Neevel, Johan G. 2002. "Im(possibilities) of the Phytate Treatment of Ink Corrosion." In Contributions to Conservation: Research in Conservation at the Netherlands Institute for Cultural Heritage (ICN), ed. Jaap A. Mosk and Norman H. Tennent, 74–86. N.p.: James & James.

Schåfer, I. 2004. "Iron Gall Ink Corroded Autographs of the 18th and 19th Centuries: Conservation of Material Characteristics Versus Conservation Treatments." Proceedings of the International Conference on Durability of Paper and Writing November 16–19. Ljubljana, Slovenia: MIP. P. 50.

Reissland, Birgit. 1999. "Ink Corrosion Aqueous and Non-Aqueous Treatment of Paper Objects—State of the Art." Restaurator 20: 167–180.

Reissland, Birgit. 2000. "Ink Corrosion: Side Effects Caused by Aqueous Treatments for Paper Objects." Postprints of the The Iron Gall Ink Meeting, Newcastle Upon Tyne, England: University of Northumbria, 109–114.

Reissland, Birgit. 2000. "Visible Progress of Paper Degradation Caused by Iron Gall Inks." Postprints of the The Iron Gall Ink Meeting, Newcastle Upon Tyne, England: University of Northumbria, 67–72.

Reissland, Birgit and Judith Hofenk de Graaff. 2000. "Condition Rating for Paper Objects with Iron Gall Ink." ICN-Information 1 (May).

Rhodes, Barbara and William Wells Streeter. 1999. Before Photocopying: The Art and History of Mechanical Copying. New Castle, DE: Oak Knoll Press & Herald Bindery.

Strlic, Matija, et al. 2003. "A Comparative Study of Several Transition Metals in Fenton-like Reaction Systems at Circum-neutral pH." Acta Chim. Slov. 50: 619–632.

Titus, Sonja, et al. 2006. "The Copy Press Process: History and Technology, Part 1." Restaurator 27 (2): 90–102.

Titus, Sonja, et. al. 2009 "Stabilising Local Areas of Loss in Iron Gall Copy Documents from the Savigny Estate." Restaurator 30 (1–2): 16–50.

Ubbink, K. and R. Partridge. 2003. Preserving Letterpress Copying Books." Canadian Association for Conservation of Cultural Property 28: 38–45.

Van der Reyden, Diane, Christa Hofmann, and Mary Baker. 1993. "Effects of Aging and Solvent Treatments on Some Properties of Contemporary Tracing Papers." Journal of the American Institute for Conservation 32 (2): 177–206.

ACKNOWLEDGEMENTS

This project was made possible by the generous support of all of the following: Will Morrison, Smithsonian Office of Fellowships; Sarah Stauderman, Collections Care Manager, Smithsonian Institution Archives; Nora Lockshin, Paper Conservator, Smithsonian Institution Archives; Anne

Van Camp, Director, Smithsonian Institution Archives; Ricardo Peñuela-Pava, Volunteer, Smithsonian Institution Archives; Jennifer Giaccai, Conservation Scientist, Museum Conservation Institute; Odile Madden, Visiting Research Scientist, Museum Conservation Institute; Elizabeth Keats Webb, Intern, Museum Conservation Institute; Karen Pavelka, Lecturer, School of Information, University of Texas at Austin; Chela Metzger, Lecturer, School of Information, University of Texas at Austin; Sheila Siegler, Paper Conservator and Conservation Scientist; Rachel-Ray Cleveland, Owner, Cleveland Conservation of Art of Paper, Inc.; Frank Mowery, Head of Conservation, Folger Shakespeare Library; Crystal Maitland, Paper Conservator, Sheridan Libraries, Johns Hopkins University; Elmer Eusman, Special Assistant to the Director for Preservation, Library of Congress; Cindy Connelly Ryan, Preservation Research and Testing Division, Library of Congress. Thank you all very much.

BETH ANTOINE
Post-Graduate Fellow in Conservation
Smithsonian Institution Archives
Washington, DC
beth@pixelfork.com

MARION MECKLENBURG
Senior Research Scientist
Museum Conservation Institute
Smithsonian Institution
Washington, DC
MecklenburgM@si.edu

ROBERT J. SPEAKMAN
Head of Technical Studies
Museum Conservation Institute
Smithsonian Institution
Washington, DC
SpeakmanJ@si.edu

MEL WACHOWIAK
Senior Conservator
Museum Conservation Institute
Smithsonian Institution
Washington, DC
WachowiakM@si.edu