2001 RELACT Series

The History and Treatment of Works in Iron Gall Ink
September 10-14, 2001, 9:30-5:30 daily
Museum Support Center
Smithsonian Center for Materials Research and Education

Instructors: Birgit Reibland, Han Neevel, Julie Biggs, Margaret Cowan
Additional Lecturers: Jacque Olin, Elissa O'Loughlin, Rachel-Ray Cleveland, Linda Stiber Morenus, Heather Wanser, Abigail Quandt, Christine Smith, Maria Beydenski, Season Tse, Elmer Eusman, Scott Homolka

This 3-day course (offered twice in one week for 2 separate groups of participants) focuses on one of the most corrosive media problems found on documents and works of art on paper. The 2-day workshop and 1 interim day of lectures cover the production of inks from historic recipes; historic drawing and writing techniques; identification, examination and classification of deterioration; and the execution of treatment options, including the use of calcium phytate solution. The interim day of lectures will feature local and international conservators' research into the history and treatment of works with iron gall ink. The course represents the first time iron gall ink has been the primary focus of an international gathering in the United States. Registration deadline for the full course is July 1 or until the course is filled with qualified applicants; for the interim day of lectures only, participants have until August 29 to register.

Limit for Interim Day of Lectures: 30
Lunch and handouts provided
Cost: $ 75.00
Registration deadline August 29

The 3-day course is fully enrolled. Places still remain for the Interim Day of Lectures.

Please contact Mary Studt, studtm@scmre.si.edu or 301-238-3700 x149 for further information and application materials.

Mary Studt
Archives Conservator
Smithsonian Center for Materials Research and Education
Smithsonian Institution

- **3-Day Course Schedule**
- **Interim Lecture Day Schedule**
- **Course Payment Information**
- **Directions to MSC/SCMRE**
- **Related Links**

3-DAY COURSE SCEDULE

Aim of this workshop is an interactive exchange of knowledge between the workshop participants. During the lectures some basic knowledge on the subject and recent developments on the subject will be provided.

DAY 1 - Iron Gall Inks: Recipes, Composition, Visual Analysis, Degradation
Lecture - *Introduction to Historical Ink Recipes* (BR)
Lecture - *Iron Gall Ink Chemistry* (HN)

BREAK

Lecture - *Visual Characteristics of Iron Gall Inks* (BR)
Practical - Producing an iron-gall ink following a historical recipe, application on different papers

LUNCH

Lecture - *Chemistry of the Ink Corrosion Process* (HN)
Lecture - *Diagnosis of Ink Corrosion - Condition Rating* (BR)
Discussion - Decision Making / Condition Rating / Priority Surveys (participants)

BREAK

Practical - Looking at Originals / Condition Rating / Iron(II) Test
Discussion

DAY 2 - Conservation Treatment of Ink Corroded Objects
Lecture - *Overview of Treatments for Ink Corrosion* (Julie Biggs)
Lecture - *Chelating-Treatment of Ink Corrosion* (HN)
Lecture - *Comparison of Aqueous Treatments for Ink Corrosion* (BR)

BREAK

Lecture - *Side Effects Caused by Aqueous Treatments* (BR)
Discussion - Case studies / interesting conservation projects (participants)

LUNCH

Practical - Making a Ca-phytate solution / iron(II)test / looking at treated originals
Lecture - *Mechanical Stabilisation of Ink Corroded Originals – Overview* (BR)

BREAK

Practical - Application of different conservation treatments including Ca-phytate (BR)
Discussion

INTERIM DAY OF LECTURE SCHEDULE

Jacque Olin: *Production of Green Vitriol (Ferrous Sulfate) in the 15th Century*
Elissa O'Loughlin: *Some Notes on Powdered Iron Gall Inks*
Rachel-Ray Cleveland: *The Ubiquitous Iron Gall Ink: Present Where You May Not Expect to Find It*

BREAK

Linda Stiber Morenus: *In Search of a Remedy: The History of Treating Iron Gall Ink at the Library of Congress*
Heather Wanser: *An Evaluation of Standard and Modified Aqueous Deacidification Treatments on Antique Iron Gall Ink; Evaluating Ethanol-Modified Magnesium Bicarbonate: its Effectiveness in Placing an Alkaline Reserve in Paper, and its Effect on Two Water Sensitive Iron Gall Inks Samples*

LUNCH

Abigail Quandt: *The Preservation and Treatment of Iron Gall Ink on Parchment*
Christine Smith: *George Washington's Last Will and Testament: Determining a Course of Treatment*
Maria Beydenski & Season Tse: *The Use of Simmering Water in the Conservation Treatment of a Nineteenth-Century Sketchbook of Iron-Gall Ink Drawings by James G. Mackay*

BREAK

Elmer Eusman: *Measuring Migrating Iron in Treated and Untreated Iron Gall Ink Samples*
Scott Homolka: *The Sensitivity of Phytate-Treated Iron Gall Ink Materials to Fungal Attack*

Panel Discussion, Questions and Answers: Birgit Reibland, Han Neevel, Julie Biggs, Lecturers

Abstract: ***Production Of Green Vitriol In The 15th Century***

Jaquie Olin, Private Researcher

My interest in green vitriol stems from the questioned authenticity of the Vinland Map. This map is in the collection of the Beinecke Library at Yale University. There is evidence to suggest that the map is a mid-15th century map. It is a map of the world, including Iceland, Greenland and Vinland. It has drawn much attention since it was purchased in 1957. Its history prior to 1957 is unknown. Publications resulting from studies of the ink of the Vinland Map have not included a discussion of ink production in the 15th century. I will present results from my research into the history of that production particularly with regard to green vitriol, the ferrous sulfate which is referred to by some as the natural product, malanterite. I will address comparisons of the published elemental analyses of the ink of the Vinland Map and the elements which this research suggests should occur with green vitriol.

Abstract: ***Some Notes on Powdered Iron Gall Inks***

Elissa O'Loughlin, Associate Conservator, The Walters Art Gallery

Iron gall inks are most often thought of as liquids. However another category of these inks exists—those made up of constituents in powdered form to which water was later added.

Manufacture, History, and Use

Powdered iron gall inks are not reconstituted inks. They were made from the basic ingredients of the wet ink formulations: a tannic source (galls), and iron source, (iron sulfate), a binder (gum arabic), and sometimes a provisional colorant (logwood). Each of the constituents were ground (or possibly precipitated) into a fine particulate, measured and then mixed together and packaged. The packets, usually made of paper, allowed the user to carry large quantities of ink without the bulk of the liquid. The ink was mixed with water as needed, and presumably formed a dark writing ink within a short period of time. Some care in formulation may have been taken to assure longevity of the powder within the paper packets. Powdered inks were taken on long journeys; Erasmus is said to have carried powdered inks with him on his travels. One could assume that they were in common use when writing materials went "on the road" with officials such as circuit court judges. Colonial American records contain many references to these inks. Benjamin Franklin sold them in his shop in Philadelphia, and the Congress of the United States purchased large quantities of the ink in paper packets.

Many questions about powdered iron gall ink could be asked. For example, if these inks were formulated for travel (consider long sea voyages) it would have been desirable that the powder maintain its dryness and not damage the paper wrappers. One extant sample of powdered iron gall ink in the U.S. National Archives (c. 1830) exhibits some properties which suggest that the form of the iron was chosen carefully. The powder is light brown-gray in color, appears finely divided (not clumped) and the particles of gum are glassy and brittle. The paper wrappers are in good condition and show no signs of damage from prolonged contact with the ink powder. In 1935 Zimmerman noted that a form of ferrous sulphate, pure heptahydrate, is not hygroscopic and does not readily oxidize in air. Could powdered iron gall inks have been made with this form of iron? Is the liquid ink made from the powdered form more or less to produce Fe++ on aging?

Although my investigations have focused on England and the American Colonies, the assumption is that powdered ink was made in other countries as well. Conservators should be alert to references of its manufacture and use elsewhere and keep in mind the need for further study of this form of our favorite ink.

Abstract: ***The Ubiquitous Iron Gall Ink: Present Where You May Not Expect to Find It***

Rachel-Ray Cleveland, Cleveland Conservation of Art on Paper, Inc., Laurel, Maryland, United States

Iron gall ink is present in some printing inks, typewriter inks, copy inks, architectural inks, and handwriting inks. In numerous cases, iron gall ink is included as a minor component in a complex ink formulation.

Even though iron gall ink may not be a typical component in ink categories described above, it is useful to know that it is sometimes present. Upon casual observation, a conservator may think that iron gall ink is not contained in various types of ink; however, the conservator is wise to anticipate the exception to the general rule.

Selected examples of iron gall ink patents and published formulations for typewriter inks, printing inks, architectural inks, copy inks, and handwriting inks will be highlighted and discussed. Because of the complexity of some ink formulations, the conservator is alerted to possible treatment complications.

Abstract: ***In Search of a Remedy: The History of Treating Iron Gall Ink at the Library of Congress***

Linda Stiber Morenus, Senior Paper Conservator, Library of Congress

From the vantage of the Library of Congress' 200 year record, we are afforded a window on the changing aesthetic, technical, and philosophical approaches to manuscript restoration and conservation. As a prominent player in the early field of preservation, the Library has been on the forefront of many major trends aimed at stabilizing paper documents, as well as those ravaged by corrosive iron gall ink.

At first the focus was on physical support for iron gall ink damaged materials. Repairs and patches with hand-made and machine-made papers of medium to tissue weight, were a common early remedy for the Library's manuscript collections.

By the mid-19th century, a diversity of transparent materials were used in the United States and Europe to reinforce iron gall ink manuscripts without obscuring the text. Tissue paper appears to have been the first material applied as an overall support. However, in 1899 the Library selected the silking process, a new technology, to arrest the increasing deterioration of its 18th and 19th century manuscripts. Unfortunatedly, the life expectancy of the silk reinforcement technique was limited to between 20 nand 30 years. As the difficiencies of silking became evident, the Library continued to search for solutions.

In 1928 the Library of Congress and the United States Bureau of Standards experimented with cellulose acetate applied as a dip coating or spray, and with cellophane as a laminating film. By 1940, these experiments, and the persuasive entreaties of William Barrow, convinced Library officials that cellulose acetate

lamination was the method of choice for supporting weak documents, including iron gall ink manuscripts.

Around this time, Barrow shifted his focus to the acidity which undermines the iron gall ink, and paper generally. In the mid-1940's, he was responsible for an innovation that involved the deacidifying of documents prior to cellulose acetate lamination. This aqueous treatment (known as the "Barrow Two-Step") involved consecutive immersions in calcium hydroxide, followed by calcium bicarbonate. As a result of the Barrow protocol, some iron gall inks bled, sank, and changed color or intensity.

In compensation for the potential risks of this treatment, which included high alkalinity (the calcium hydroxide could reach pH 12.5), Barrow promoted the use of magnesium bicarbonate in the 1960's (know as the "Barrow One-Step").

While the scientific community extolled the benefits of deacidification in general, Library conservators experienced a host of deleterious side effects from treatment with Barrow's magnesium bicarbonate, including some of the same alterations to iron gall ink observed with the "Barrow Two-Step". Consequently, for the past three decades, Library conservators have modified magnesium bicarbonate with various dilutions of deionized water and/or ethanol. Non-aqueous deacidification methods have been applied to treat especially water soluble iron gall ink, as well.

Today, the Conservation Division staff is greatly interested in the promise of the calcium phytate treatment proposed by Han Neevel and Birgit Reissland. The Library is poised to begin further testing and evaluation of the calcium phytate techniques before assimilating it into common conservation practice, and is interested in coordinating its experiments with the relevant initiatives underway in other laboratories.

Abstract: ***An Evaluation of Standard and Modified Aqueous Deacidification Treatments on Antique Iron Gall Ink***
Heather Wanser, Senior Paper Conservator, Library of Congress

Research has demonstrated that an alkaline reserve can protect paper from degradation by the acids in iron gall ink. However, some conservators are reluctant to deacidify iron gall ink manuscripts aqueously out for fear that the inks might be visually altered. Spot testing does not always accurately predict treatment outcome. Thus many conservators believe that the practice of aqueous deacidification is not without risk.

The purpose of this study was to see if modifications to the customary practices used to aqueously deacidify 18th and 19th century iron gall ink documents showed any promise in reducing the incidence and degree of undesirable visual change in the ink. Six expendable 18th and early 19th century iron gall ink manuscripts were cut into a number of strips and processed through a variety of treatment solution, some of which were modified by the addition of ethanol. The treatment samples were evaluated visually in a blind comparison, by the paper conservators at the Library of Congress. Visual observations of the change in the ink were broken down into three categories: "no change", "acceptable change" , and "unacceptable". The category " acceptable change" was defined as having no obvious change to the ink, but having

a subtle color shift, perhaps due to the lightened paper beneath the ink. One interesting finding was that perceptions among the conservators varied. For example, the designations of “no change” or “unacceptable” were given to the same sample. Another aspect of this experiment was to determine to what extent customary spot testing practices are an accurate predictor of treatment outcome.

The limited supply of naturally aged 18th and 19th century documents and the resulting small sample size dictated the design of this experiment and the analysis of the results was made accordingly. Therefor this study is not definitive, although thought provoking and a springboard for further investigations. This presentation will share the results of the comparison of the treated samples, and the accuracy of spot testing.

Abstract: ***Evaluating Ethanol-Modified Magnesium Bicarbonate: its Effectiveness in Placing an Alkaline Reserve in Paper, and its Effect on Two Water Sensitive Iron Gall Inks***

Heather Wanser, Senior Paper Conservator, Library of Congress

Numerous documents contain water soluble inks that prevent them from being washed and deacidified in aqueous systems. Conservators often modify the traditional aqueous treatments by adding a portion of ethanol to the wash baths or the aqueous deacidification solutions in order to reduce the chance of adversely effecting water sensitive media. However, no study has established the amount of alkaline reserve deposited in paper when the deacidification solution was modified by using 50% or 65% ethanol.

Three different types of paper (newsprint, pure rag, and an 18th-century text block) were processed through one of three solutions: aqueous, 50% and 65% ethanol modified, each containing the same percentage of magnesium bicarbonate. The alkaline reserve in each paper was measured by pH (both surface and cold water extraction), and by alkaline reserve measurements obtained through back titration.

The effect of these same solutions on two naturally aged, 18th century, water sensitive iron gall inks were also evaluated. The samples were cut into strips, variously treated as above, and the results evaluated visually by conservators in a blind comparison.

This study provides conservators with a better understanding of the use of ethanol modified aqueous deacidification treatments for documents with water sensitive media.

Abstract: ***The Preservation and Treatment of Iron Gall Ink on Parchment***

Abigail Quandt, Senior Paper Conservator, The Walters Art Gallery

The author will touch on some case histories, discuss consolidation treatment, and then finish with a discussion of the imagining and conservation work presently being performed on the Archimedes Palimpsest at the Walters Gallery.

Abstract: ***George Washington's Last Will and Testament: Determining a Course of Treatment***

Christine Smith, Chief Conservator and President, Conservation of Art on Paper Inc.

George Washington's profoundly moving last will and testament can be considered his last message to the American people. Written in iron gall ink on both sides of twenty-two sheets of stationery, the manuscript suffered Civil War damage that led to a masterful restoration by William Berwick in 1910. Ninety years later, Mr. Berwick's silking and binding treatment required conservation, and research reported from ongoing projects in The Netherlands offered considerable guidance in determining a course of treatment. However, exactly how to proceed had to be decided by weighing the need for treatment, philosophical treatment questions, unanswered questions about the nature of iron gall ink, and the previous restoration.

Abstract: ***The Use of Simmering Water in the Conservation Treatment of a nineteenth-Century Sketchbook of Iron-gall Ink Drawings by James G. Mackay***

Maria Bedynski, Paper Conservator, National Archives of Canada
Season Tse, Conservation Scientist, Canadian Conservation Institute

The National Archives of Canada houses the largest and important collection of sketchbooks and albums containing works by either Canadian artists or those depicting Canadian landscape and life of this country's past and present inhabitants.

The James G. MacKay sketchbook titled: The Pilgrim's Progress Colored is a parody of John Bunyan's Pilgrim's Progress, narrating the misadventures of a poor black Mr. Christian within a Canadian context. The sketchbook dates from the mid-nineteenth century and is fairly typical of blank note books available at the time. It is filled with iron-gall ink and pencil drawings that are severely damaged by ink corrosion. The iron-gall ink was determined to be both corrosive and acidic and has resulted in the discolouration of the paper support, numerous fractures and losses and the offsetting of images, particularly in heavily inked areas. This condition prevented the sketchbook from being studied, consulted and copied since it was acquired by the National Archives in 1988.

To facilitate access, the sketchbook needed to undergo conservation treatment that would strengthen the brittle paper support, reduce discolouration, stabilize fragile areas and arrest the ink corrosion. To assist in the choice of treatment for this sketchbook, the Canadian Conservation Institute's Analytical Research Services Laboratory was asked to carry out analysis of the paper fibre content, fillers and size used in the paper along with compositional analysis of the ink.

Two different treatments were considered for the MacKay sketchbook; the recently developed at the Netherlands Institute for Cultural Heritage, calcium phytate treatment, and the "boiling", or as we prefer to call it, "simmering" water treatment, that is based on the experiments of Austrian conservators and treatments carried out in a few European laboratories since the 1970s. The benefits and risks of each mentioned treatment were carefully analysed and discussed amongst the curator, archivist and paper conservators at the National Archives and conservators and conservation scientists at the Canadian Conservation Institute. In the end, we all agreed that the MacKay sketchbook should be treated using simmering water.

Prior to the treatment carried out at the National Archives, two single pages and one folio from the MacKay sketchbook were brought and treated at the Canadian Conservation Institute on March 1, 2001. The treatment involved simmering the selected pages in two separate baths, for 15 minutes. Water samples were collected at 0, 2, 4, 6 10 and 15 minutes from each of the two treatment baths. Dissolved metals in the wash water was analysed using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP/AES). ICP scan for 36 metals, pH and UV/Visible Spectrophotometric analyses were carried out for all wash water samples.

The paper will discuss the physical and chemical condition of the drawings in the MacKay sketchbook before and after the simmering water treatment, including analysis of the materials and results of wash water analysis. The difficult process of choosing the optimal treatment and its ethical significance will be addressed along with a "step-by-step" description of the treatment.

Abstract: ***Measuring Migrating Iron in Treated and Untreated Iron Gall Ink Samples***

Elmer Eusman, Senior Paper Conservator, Library of Congress

In a research project that was initiated by the Boijmans Museum in Rotterdam and sponsored by the Shell Research and Technology Centre in Amsterdam (SRTCA) various samples containing iron gall ink were examined specifically for the iron content in and outside of the applied ink line. The samples were examined using a non-bleeding Fe2+ test, developed by Han Neevel at the Netherlands Institute of Cultural Heritage (ICN), and SEM/EDX analysis at the SRTCA facilities.

Naturally aged samples from various late 19th century papers were treated in different ways to examine the effect of the treatment on the potential migration of the ink into the surrounding paper. The treatments included various humidification and washing methods. Two sets of samples were aged artificially to explore a direct relationship between migrating iron and potential discoloration of the regions directly outside of the ink line.

The non-bleeding Fe2+ test proved to be a safe and useful tool for both examining migration of iron in the ink samples as well as for indicating the presence of Fe2+ in the washing solution in which the ink samples had been treated. Washing the samples in water almost always diminished the Fe2+ content in the ink regions while adding ethanol to the washing solution generally resulted in less removal of Fe2+ from the ink samples. This was not only visible from the Fe2+ content in the ink region but also from Fe2+ in the washing solution. Despite the proven presence of Fe2+ in the washing solution the washed samples from this project did not show increased amounts of iron in the non-inked regions after treatment.

The majority of the humidified samples showed loss of iron in the inked regions but the Fe2+ test rarely showed the presence of Fe2+ outside the ink line. However, SEM/EDX analysis confirmed the notion that humidification of iron gall ink on paper can very easily result in the migration of iron. Reaffirming the threat of migrating iron during humidification was the observation that contrary to the untreated and washed samples the humidified samples showed substantial discoloration around the inked regions after artificial aging.

Abstract: ***The Sensitivity of Phytate-Treated Iron Gall Ink Materials to Fungal Attack***
Scott Homolka, Graduate Intern,

Iron gall ink corrosion has spurred much recent research in the field of paper conservation. It causes deterioration of the paper substrate by two main processes, acid hydrolysis and oxidative cleavage. During oxidative degradation, iron(II) ions from the ink catalyze the formation of organic radicals and hydrogen peroxide which is decomposed further to form highly reactive hydroxyl radicals. Aqueous treatments have been designed to slow the attack of iron gall ink on the paper substrate. One of the most promising treatments involves the use of a calcium or sodium phytate solution to complex iron(II) ions into iron(III) phytate, thus inhibiting radical formation. The concern has been voiced, but not yet investigated experimentally, that phytate-treated materials may exhibit an increased susceptibility to fungal growth, especially in high relative humidity environments. This paper presents an experimental procedure designed to investigate the relationship between phytate-treated iron gall ink materials and fungal growth.

Directions to SCMRE
By Car: Check http://www.si.edu/scmre/about/driving.htm for driving directions to MSC/SCMRE.

By Metro: Take the Suitland stop from the green line:
http://www.wmata.com/metrorail/systemmap.htm,
http://www.stationmasters.com/System_Map/SUITLAND/suitland.html.
Walk west on Silver Hill about ½ mile to the Smithsonian Museum Support Center, on the north side of the street.

By Shuttle: Check http://www.scmre.org/01.html for a schedule and stop locations on the Smithsonian Mall.

Course Payment Information
Payment should be made by check or money order to the Smithsonian Institution. Please write the course number and title onto the check or money order. Send payment to SCMRE-COURSES, MSC-SI MRC-534, 4210 Silver Hill Road, Suitland, Maryland 20746. For additional payment information, contact Francine Lewis, 301-238-3700, x102.

Related Links

the iron gall ink corrosion website

On-line Conservation Articles with references to iron gall ink:

Identification:

- An Investigation Toward the Identification of Traditional Drawing Inks
- Pigment Analysis of Early American Watercolors and Frakturs

Fixative Application:

- Cyclododecane: Technical Note on Some Uses in Paper and Objects Conservation

Washing, Mending, Lining, Desilking Treatments of Works with Iron Gall Ink:

- The Core Collection of the Manuscript Division at the Library of Congress
- Sprayed Poly (vinyl acetate) Heat Seal Adhesive Lining of Pen and Iron Gall Ink Drawings on Tracing Paper
- The Examination and Conservation Treatment of the Library of Congress Harkness 1531 Huejotzingo Codex

Housing and Transport of Works with Iron Gall Ink:

- The Bill of Rights Goes to Spain

Line and Shadow: The Role of Ink in American Architectural Drawings Prior to 1860