SYLVIA ALBRO, JULIE L. BIGGS, CLAIRE DEKLE, MARY ELIZABETH HAUDE,
CYNTIA KARNES, AND YASMEEN KHAN

Developing Guidelines for Iron-Gall Ink Treatment at the Library of Congress

The Library of Congress Conservation Division formed a working group to establish protocols for iron-gall ink treatment as part of a multi-year commitment by the Preservation Directorate to address the conservation and preservation of iron-gall ink. The group's goal was to evaluate existing Conservation Division practices together with recent research and produce a set of guidelines for staff to use in the examination and treatment of iron-gall ink on paper.

Iron-gall ink is well represented in collections at the Library of Congress. The Manuscript Division in particular holds many important documents written in iron-gall ink by the founders of the United States. In addition, iron-gall ink is abundantly represented in maps and atlases in the Geography and Map Division; art and architectural drawings in the Prints and Photographs Division; scores by famous composers in the Music Division; and ancient manuscripts in the African and Middle Eastern Division.

Various treatments have been utilized to combat the damaging effects of iron-gall ink corrosion on works in the Library's collection. From the late-nineteenth century through the mid-twentieth century, treatments, such as lining, silking and lamination with cellulose acetate, largely focused on reinforcing paper weakened by iron-gall ink corrosion. However well intended, these treatments did not address corrosion of the ink itself; in fact, they often accelerated the deterioration of the ink and paper.

In the last ten to fifteen years, researchers in Europe have elucidated the deterioration mechanisms associated with iron-gall ink and have developed new examination tools and treatment options for its stabilization (Banik and Webber 1999; Brown 2000; Kolar and Strlič 2006). In 2001, the Library of Congress initiated its own research project and established the Iron-Gall Ink Corrosion Group to investigate the efficacy of existing treatments conducted by the Library's conservation staff alongside recently developed European treatments.

Independent submission. Paper not presented at 2008 AIC meeting.

In 2005, when the Iron-Gall Ink Corrosion Group had completed its work, a second group was formed to develop a unified approach toward preserving Library collections incorporating iron-gall ink. The Protocols for Iron-Gall Ink Treatment (PIT) Group developed a set of written guidelines for the examination, documentation and treatment of iron-gall ink on paper. This was accomplished by integrating the Library of Congress study (Connelly-Ryan et al. 2007) and published research with findings documented in internal treatment records, anecdotal observations and experiences of staff conservators, and discussions with colleagues outside the Library. The guidelines were evaluated and refined through a series of practical demonstrations and in dialogue with conservation staff.

The effort highlighted the need for further research to verify and build upon existing studies; in particular, to evaluate the long-term effects of ethanol-modified treatments; magnesium-based complexing and alkaline treatments; and different types of sizing agents on iron-gall ink.

The documents reproduced in the following pages represent a comprehensive effort to guide the conservator through myriad options for the preservation and conservation of iron-gall ink on paper. While these guidelines are specifically designed for objects at the Library of Congress that reside in optimal storage and environmental conditions, the approach may be customized to suit the particular needs of diverse collections and institutions. The guidelines comprise nineteen documents: a detailed examination form designed specifically for iron-gall ink on paper to supplement the primary record of treatment; a glossary that standardizes the terminology used in the examination form; recommendations for micro-chemical and solubility testing; a system of flow charts, or "treatment trees", to guide the decision-making process based on results obtained through examination and testing; and explanatory notes on the treatment options presented. New research and information will be incorporated into the guidelines in the future as the opportunity arises.

The documents are presented here as a contribution to the national and international dialogue on the treatment of iron-gall ink. A detailed explanation of the treatment trees is given in the postprints of the International Institute of Paper Conservation/Institute of Conservation conference held in Edinburgh in July 2006 (Biggs et al. 2007). The practical application of the guidelines to the complex treatment of three important Library of Congress objects is presented in the succeeding article, "Iron-Gall Ink Treatment at The Library of Congress: Old Manuscripts—New Tools", by Claire Dekle and Mary Elizabeth Haude.

GUIDELINE DOCUMENTS FOR THE EXAMINATION AND TREATMENT OF IRON-GALL INK ON PAPER

On the following pages find these documents

Examination and Testing (5 documents)
- Record of Examination of Iron-Gall Ink on Paper (fig. 1)
- Additional Testing (fig. 2)
- Glossary for Record of Examination of Iron-Gall Ink on Paper (fig. 3)
- Chemical Testing (fig. 4)
- Solubility Testing (fig. 5)

Treatment Trees (2 charts)
- Washing Treatment Trees (fig. 6)
- Alkaline & Complexing Treatment Trees (fig. 7)

Washing and Drying Treatments (6 documents)
- Conditioning / Pre-Wetting (fig. 8)
- Water Type (fig. 9)
- Water Temperature (fig. 10)
- Washing Methods (fig. 11)
- Ethanol-Modified Washing (fig. 12)
- Drying (fig. 13)

Alkaline and Complexing Treatments (6 documents)
- Bookkeeper ® Spray System (fig. 14)
- Calcium Bicarbonate (fig. 15)
- Calcium Phytate / Calcium Bicarbonate (fig. 16)
- Ethanol-Modified Calcium Phytate / Calcium Bicarbonate (fig. 17)
- Magnesium Bicarbonate (fig. 18)
- Ethanol-Modified Magnesium Bicarbonate (fig. 19)

Sizing (1 document) (fig. 20)

REFERENCES

Banik, G. and H. Webber, eds.1999. *Tintenfraßschäden und ihre behandlung*. Stuttgart: W. Kohlhammer GmBH.

Biggs, Julie L., et al. 2007. Treatment trees for iron-gall ink on paper: Using flow charts to develop treatment protocols. In *Edinburgh Conference Papers 2006*, ed. Shulla Jaques. London: Institute of Conservation. 211–218.

Brown, Jean A., ed. 2000. *The iron gall ink meeting*. Newcastle upon Tyne, 4th & 5th September: Postprints, The University of Northumbria.

Connelly-Ryan, Cindy, et al. 2007. Optimizing ink corrosion treatment protocols at the Library of Congress. In *Edinburgh Conference Papers 2006*, ed. Shulla Jaques. London: Institute of Conservation. 195–202.

Kolar, J. and M. Strlič, ed. 2006. *Iron gall inks: On manufacture, characterisation, degradation and stabilization*. Narodna in Univerzitetna Knjižnica, Ljubljana.

SYLVIA ALBRO
Senior Paper Conservator
The Library of Congress
Washington DC
salb@loc.gov

JULIE BIGGS
Senior Paper Conservator
The Library of Congress
Washington DC
jubi@loc.gov

CLAIRE DEKLE
Senior Book Conservator
The Library of Congress
Washington DC
cdek@loc.gov

MARY ELIZABETH HAUDE
Senior Paper Conservator
The Library of Congress
Washington DC
mhaud@loc.gov

CYNTIA KARNES
Senior Paper Conservator
The Library of Congress
Washington DC
ckarnes@loc.gov

YASMEEN KHAN
Senior Book Conservator
The Library of Congress
Washington DC
ykha@loc.gov

FIG. 1.1

RECORD of EXAMINATION of IRON-GALL INK on PAPER
Library of Congress – Conservation Division

project number

examination date

author / artist / maker

title

date

description of object

conservator

APPEARANCE of INK

Color	warm / cool	pale / dark
	[describe - hue, etc.] _____	
Intensity	light / medium / strong / other _____	
Application	quantity	uniform / variable
	quality	soft / sharp / feathered / wash / smeared
Penetration	none / slight / moderate / severe / cannot determine	
Surface characteristics	shiny / dull	
	particulate	no / yes [describe] _____
	deposits [describe] _____	
Other		

CONDITION of INK and PAPER (Note: numerals correspond to Treatment Trees)

VISIBLE LIGHT

1	Physical damage to inked paper	cracks	none / some / many
		losses	none / some / many
		delamination	none / slight / moderate / severe
		other [describe] _____	
2	Discoloration surrounding ink		none / overall / localized [describe] _____
			slight / moderate / severe
	Adhesion / Cohesion	friability	none / overall / localized [describe] _____
			slight / moderate / severe
		cupping	none / overall / localized [describe] _____
			slight / moderate / severe
		cracking	none / overall / localized [describe] _____
			slight / moderate / severe
		flaking	none / overall / localized [describe] _____
			slight / moderate / severe
3	Burn-through		none / minor / moderate / severe
	Transfer of discoloration	no / yes	[location, describe] _____

ULTRAVIOLET LIGHT (longwave, 364-365 nm)

Absorption	none / overall / localized [describe] _____	
4 Fluorescence	none / overall / localized [describe] _____	
	location [describe] _____	color [describe] _____
Other		

CHARACTERISTICS of PAPER

Opacity	translucent----------opaque
Thickness	_____ millimeters
Surface texture	smooth----------rough
Degree of sizing	not sized----------heavily sized
Other relevant observations	

FIG. 1.2

CHARACTERISTICS of ATTACHMENTS / ASSOCIATED MATERIALS **(e.g. seals, ephemera)**

locations(s)

[describe]

Appearance in ultraviolet light (longwave, 364 – 365 nm)

Sensitive? water _____

pH _____

bleeding
sinking
surface change
color change
color separation
transfer / offsetting

TESTING Record locations, duration and results of testing. Possible results may include .....

	location	BEFORE	DURING	AFTER
CHEMICAL Iron (II) ion				
pH of paper surface [test mfr.] _____				
other (e.g. iron (III) ion, copper)				
RATE of ABSORPTION by PAPER				
SOLUBILITY				
H_20 filtered / deionized alkalized w/ _____ to pH _____				
Ethanol				
Ethanol & deionized H_20 solution alkalized w/ _____ to pH _____ _50%_ / _50%_				
____ / ____				
Alkaline or complexing solutions _____ _____				

SUMMARY

FIG. 2

RECORD of EXAMINATION of IRON-GALL INK on PAPER
Library of Congress – Conservation Division

project number

examination date

ADDITIONAL TESTING	Record locations, duration and results of testing. Possible results may include: bleeding, feathering, sinking, surface change, color change, color separation or transfer of ink components to test material			
	LOCATION	BEFORE	DURING	AFTER
CHEMICAL Iron (II) ion				
pH of paper surface [test mfr.] _____				
other (e.g. iron (III) ion, Cu)				
RATE of ABSORPTION by PAPER				
SOLUBILITY H_20 filtered / deionized				
alkalinized w/ _____ to pH _____				
Ethanol				
Ethanol & deionized H_20 solution				
alkalized w/ _____ to pH _____				
_50% / 50%_				
____ / ____				
____ / ____				
Alkaline or complexing solutions				
_____				
_____				

PROTOCOLS for IRON-GALL INK TREATMENT NOTES **FIG. 3.1**
Library of Congress – Conservation Division

GLOSSARY for RECORD of EXAMINATION of IRON-GALL INK on PAPER

The glossary defines and elaborates terms used in the "Record of Examination of Iron-Gall Ink on Paper"

APPEARANCE of INK This section records observations about the visual character of the ink.

Color Describes the hue of the ink and whether it is **warm** or **cool, pale** or **dark**.

Intensity Describes the strength or opacity of the ink, judged by its ability to obscure the paper.

Application Describes observations of the method(s) used to deposit ink on the paper.

Quantity Describes the amount of ink deposited by the tool used to apply the ink. For example, the quantity of ink applied with a quill pen is likely to be **variable** as the pen is used and recharged. A fountain pen is likely to produce a more **uniform** line as ink is continuously released from the ink reservoir.

Quality Describes characteristics imparted to the ink during its application.

Soft and **sharp** describes the edge definition of an ink line.
Feathered ink is the result of ink moving laterally through the paper.
Wash refers to application by brush, often indicated by the presence of large areas of ink and a softer, wider line than could be achieved with a writing instrument.
Smeared refers to inadvertent movement of ink before it is completely dry.

Penetration Refers to the degree to which the ink moved into the paper upon application. Characteristics of both the ink and the paper affect the penetration, such as the dye-like qualities of the ink, the amount of binder in the ink, and the porosity of the paper.

Surface characteristics **Shiny or dull** refers to the appearance of the ink as a function of its ability to reflect or scatter light. The assessment is best judged with magnification. The degree of reflectance or scatter is influenced by the binding medium, the penetration of ink into the paper, and the presence or absence of particulates.
Particulate describes the presence of colored, opaque solids, generally formed by oxidation of the ink before drying.
Deposits refer to substances found on the surface of the ink but not integral to it, such as crystals or exudates. These deposits are the products of chemical reactions in the ink film; they are not to be confused with sand or other particles applied to help dry the ink.

CONDITION of INK and PAPER This section records observations related to the degradation of ink.

Physical damage to inked paper Describes physical damage to the paper as a direct result of ink corrosion.
Cracks are breaks through the ink and paper.
Losses are holes in inked areas of paper.
Delamination describes an inked layer of paper splitting or peeling away from the main body of the paper.

Discoloration surrounding ink Describes diffuse, darkened areas of paper surrounding ink applications.

PROTOCOLS for IRON-GALL INK TREATMENT NOTES **FIG. 3.2**
Library of Congress – Conservation Division

GLOSSARY for RECORD of EXAMINATION of IRON-GALL INK on PAPER

Adhesion/ Cohesion

Adhesion refers to the degree to which the ink holds onto the paper.
Cohesion refers to the degree to which components of the ink hold together.

Friability describes the loss or deterioration of the ink binder, sometimes indicated by the transfer of a fine particulate to adjacent areas. Evaluated with a microscope, ink is considered friable if particles are readily moved with the light touch of a brush or feathered blotter edge.
Cupping describes severe cracking that indicates physical stresses in the ink layer. It is usually visible as "islands" of ink, with lifted edges.
Cracking describes the formation of fissures in the ink layer, not in the paper.
Flaking describes detachment of ink from the paper.

Burn-through Refers to the darkening on the verso of an inked area caused by ink corrosion rather than ink penetration. Other physical damage to the paper may be associated with burn-through, especially if it is severe. Sometimes referred to as "strike-through", a term borrowed from printing.

Transfer of discoloration Indicates localized darkening of paper in contact with the inked paper. The discoloration is a mirror image of the original inked area, generated through chemical reactions. The phenomenon may be apparent as fluorescence in ultraviolet (UV) radiation, as well as discoloration in visible light.

Absorption Indicates the presence of iron based on its characteristic absorption of UV wavelengths. Absorption is a useful indicator, rather than an absolute identifier for iron, as other metals also absorb UV. UV enhances the visibility of iron dispersed in paper that might not be apparent in visible light.

Fluorescence Indicates paper degradation visible around the inked area or in paper in contact with the ink. May be a precursor to **discoloration**. Fluorescence is often more apparent on the verso rather than the recto of paper.

CHARACTERISTICS of PAPER This section records paper characteristics that particularly affect the deposition and appearance of the ink.

Opacity An estimation of the ability of light to pass through paper. Mark the dotted line of the scale between **translucent** and **opaque**. Tracing paper is an example of translucent paper; thick blotting paper is an example of opaque paper.

Thickness A measurement of the paper in cross-section, made with a micrometer.

Surface texture A description of the visual or tactile qualities of the paper. Mark the dotted line of the scale between **smooth** and **rough**. An example of **smooth** paper is a hot pressed or calendared sheet; an example of **rough** paper is a heavily textured watercolor paper.

Degree of sizing An assessment of the deposition of the paper size. Mark the dotted line of the scale between **not sized** and **heavily sized**.

PROTOCOLS for IRON-GALL INK TREATMENT NOTES **FIG. 4**
Library of Congress – Conservation Division

CHEMICAL TESTING

Iron (II) Ion

Iron (II) ions catalyze oxidative degradation of cellulose, one of the primary destructive reactions associated with iron-gall ink on paper.

An indicator paper developed by the Netherlands Institute for Cultural Heritage may be used to test for the presence of iron (II) ions. The test paper is made of Whatman® filter paper impregnated with an iron (II) sensitive compound, bathophenanthroline. When moistened with deionized water and placed in direct contact with iron gall ink, the indicator paper turns magenta or pinkish-red in response to iron (II) ions. The color may be evaluated semi-quantitatively to determine the presence of iron (II) ions in the ink and paper before and after treatment.

Iron (III) Ion

If the iron (II) test is negative, a test for the presence of iron (III) ions should be performed. Iron (III) ions can be reduced to iron (II) ions through redox reactions and cause oxidative degradation of cellulose.

The test paper from the iron (II) test kit is moistened with de-ionized water and placed in direct contact with iron-gall ink. After the test paper is removed from the object, a drop of 1% aqueous ascorbic acid solution is applied to the test paper. As the ascorbic acid reduces iron (III) ions to iron (II) ions, the indicator paper will turn magenta or pinkish-red.

pH

Although surface pH is only an approximate measurement of the true pH of the paper, it is a useful indicator of the efficacy of treatment. Surface pH can be measured using non-bleeding pH indicator strips and surface-electrode pH meters. pH strips are preferable to pH meters for use on objects because they require less moisture. Reducing the amount of moisture reduces the risk of ink movement, iron ion migration, tidelines, and paper distortion.

pH strips are composed of paper impregnated with a color-sensitive acid-base indicator designed to respond within a discrete pH range. Since the pH measurements of iron-gall ink are generally between 1.0 and 4.0, it may be helpful to start testing with a pH strip for that range. To further reduce the amount of moisture applied to the object and to conserve resources, a pH strip may be cut into several, more narrow strips.

SOURCES CONSULTED

Biggs, Julie L. 2006. The conservation of iron-gall ink on paper. *Working paper*. FAIC Samuel H. Kress Conservation Publication Fellowship.

Neevel, Johan G., and Birgit Reißland. 2005. Bathophenanthroline indicator paper development of a new test for iron ions. *PapierRestaurierung* 6 (1): 28-36.

PROTOCOLS for IRON-GALL INK TREATMENT NOTES **FIG. 5.1**
Library of Congress – Conservation Division

SOLUBILITY TESTING

Test Objectives

- To predict ink solubility in proposed treatment solutions. Since solubility parameters of inks treated with partially aqueous solutions might change, retesting of water-sensitive inks is recommended between treatment steps.
- To predict potential for color change in ink and paper
- To predict potential for movement of ink to verso (sinking) and lateral spread (bleeding)

Test Site Selection and Documentation

- Test each type of ink apparent throughout the object. Indications that different inks may have been used include variations in handwriting, the use of correction or deletion marks, the presence of annotations, addresses or signatures, or if the object has many pages or spans many years. The most sensitive or soluble ink will determine the treatment approach.
- Test inks that exhibit evidence of differential aging, whether due to discrete variations in storage conditions or local treatment. Indications of such variation may be more apparent in ultraviolet or infrared wavelengths.
- Perform tests in an inconspicuous area where possible
- Test in an uninked area of paper and compare with ink results to determine the degree to which any discoloration is contributed by the paper
- Become familiar with the appearance of the recto and verso of areas just before testing
- Annotate/mark blotters or other testing materials during treatment to refer to until treatment is completed.
- Make a photocopy of the object, sleeved in polyester film, to note locations of testing sites. Note type/method of test performed. If photocopying is not advisable, note locations on a polyester template using indelible marker.

Test Solutions and Sequencing

- It is advisable to perform treatment as soon as possible after testing
- Initial tests should be very small, using the aid of a magnifier or microscope to assess change
- Where possible, use test solutions and methods that will mimic proposed treatment conditions. This may include adjustments to pH, choice of treatment solutions, temperature, duration, or method of application (such as using a suction table).
- Placing a moisture barrier below the test site encourages movement of the solution upward or laterally. Placing a blotter beneath the test site encourages downward movement of the solution.
- Test with a 100% aqueous solution and 100% ethanol. If an ink is soluble in one solvent but not the other, test with varying proportions of ethanol and water to determine the solubility parameter.
- Begin testing with a droplet of solution followed by immediate blotting
- Test with alkaline and/or complexing solutions after washing and drying. If the condition of the object precludes an intermediate drying step, test with washing, alkaline and/or complexing solutions in a continuous series to mimic the proposed treatment protocol.
- As confidence grows that the ink is stable, a timed exposure may be performed by dampening the ink with repeated brush applications, wicks of cotton, or by using tiny blotter squares covered with a moisture barrier.
- Test solutions should be applied for a minimum of 12 minutes. Some changes may not be immediately visible, but may appear after 5 or 10 minutes.
- Drying may include air drying, or blotting with filter paper or blotter, using finger pressure or weight. Note that air drying, or prolonged exposure to a solution without blotting, may produce tidelines that can become stubborn stains upon aging.
- To avoid leaving visible tidelines in the paper, use methods to diffuse the edges of the tideline

PROTOCOLS for IRON-GALL INK TREATMENT NOTES **FIG. 5.2**
Library of Congress – Conservation Division

SOLUBILITY TESTING

Test Observations

- Evaluate test sites in visible light and ultraviolet radiation, and with magnification
- Note changes in ink color, texture, or intensity
- Note any changes in paper color or texture
- Look for any movement of ink to the verso (sinking)
- Note any lateral movement of ink, such as bleeding
- Compare the appearance of the test site with the surrounding paper
- Note any transfer of colored components from ink and/or paper onto blotter or wicks

WASHING TREATMENT TREES

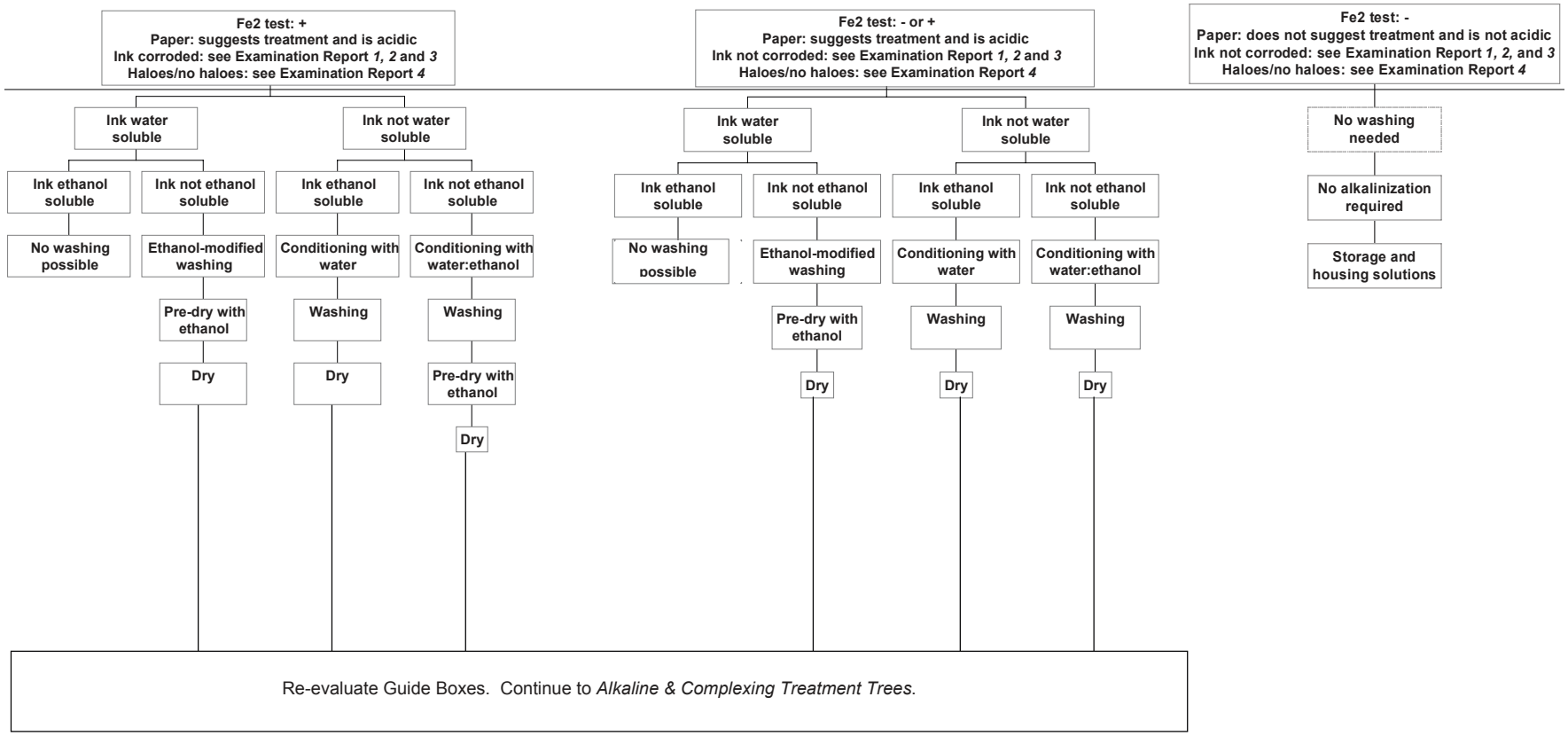

FIG. 6

ALKALINE & COMPLEXING TREATMENT TREES

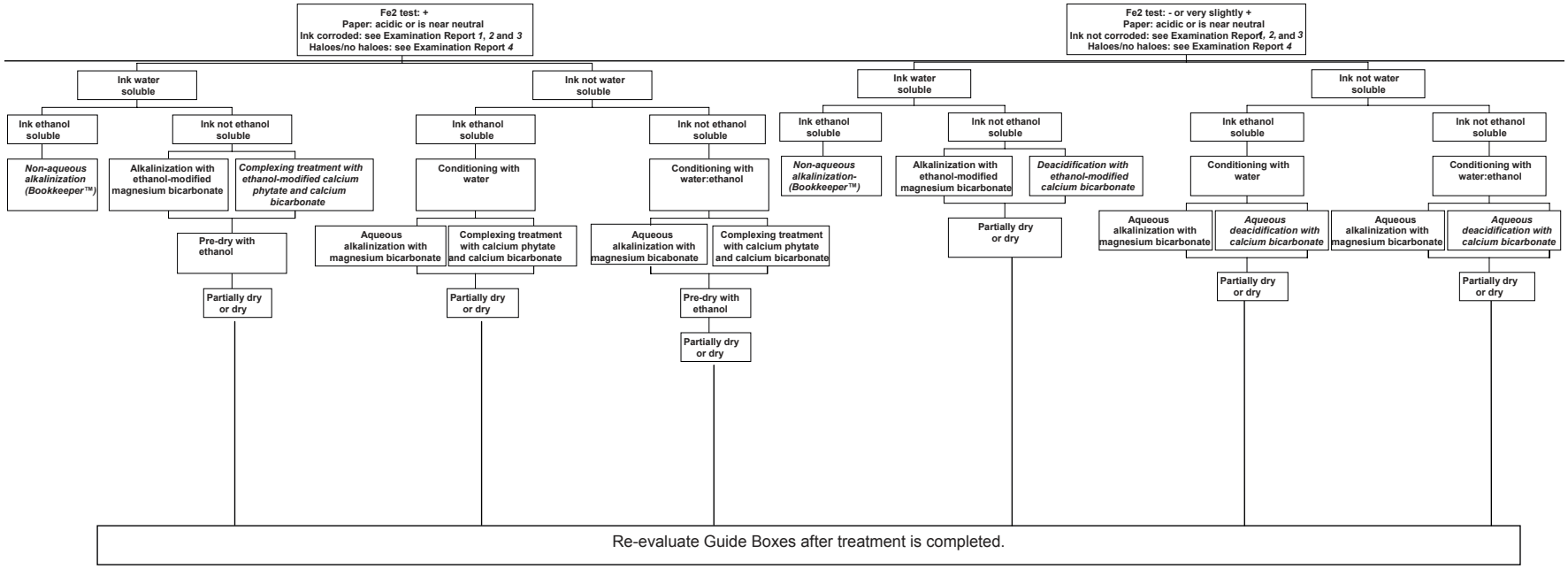

FIG. 7

PROTOCOLS for IRON-GALL INK TREATMENT NOTES **FIG. 8.1**
Library of Congress – Conservation Division

CONDITIONING / PRE-WETTING

Conditioning / Pre-wetting, general

Advantages

- Helps ensure that the ink-inscribed paper takes up moisture uniformly and does not distort during treatment
- Allows the paper fibers to swell gradually with moisture

Disadvantages

- Ink components may sink or migrate into the paper. The probability for migration may be predicted through careful testing.

Ethanol or ethanol and water solutions

Advantages

- Reduces differences in moisture absorption rates often associated with degraded sizing, or damage induced by mold or degraded ink
- Encourages the gradual replacement of ethanol with water, resulting in less distortion of paper

Disadvantages

- Ink components may sink or migrate into the paper. The probability for migration may be predicted through careful testing.
- Using ethanol requires additional precautions for health and safety

Application methods for ethanol or ethanol and water solutions

Spray

Advantages

- Ease of application
- Minimizes physical contact with the ink and/or paper
- Allows for gradual introduction of the conditioning solution

Disadvantages

- Repeated spraying may be necessary if the solution evaporates faster than the paper can absorb it

Brush

Advantages

- Ease of application
- Quickly saturates the paper with the conditioning solution. Polyester web may be used as a barrier to minimize disruption of fragile ink areas.

Disadvantages

- Use of polyester web obscures ink behavior

Bath

Advantages

- Completely and evenly saturates the paper, promoting uniform uptake of the treatment solution

Disadvantages

- Ink components may sink or migrate into the paper. The probability for migration may be predicted through careful testing.

PROTOCOLS for IRON-GALL INK TREATMENT NOTES **FIG. 8.2**
Library of Congress – Conservation Division

CONDITIONING / PRE-WETTING

Aqueous conditioning (suitable for inks that are ethanol-soluble, as ethanol-water solutions are preferred for all other conditioning/pre-wetting)

Advantages

- Reduces differences in moisture absorption rates often associated with degraded sizing, or damage induced by mold or degraded ink

Disadvantages

- Ink components may sink or migrate into the paper. The probability for migration may be predicted through careful testing.
- Hydrophobic areas of paper respond more slowly to aqueous conditioning, and may not wet up at all

Application methods for aqueous conditioning

Spray

Advantages

- Ease of application

Disadvantages

- Repeated spraying may be necessary if areas of the paper resist uptake of moisture

Humidification (damp pack or humidity chamber)

Advantages

- Allows for gradual introduction of moisture into paper. Reduces differences in moisture absorption rates often associated with degraded sizing, or damage induced by degraded ink or mold.

Disadvantages

- Ink components may sink or migrate into the paper. The probability for migration cannot be predicted, even with careful testing.

PROTOCOLS for IRON-GALL INK TREATMENT NOTES **FIG. 9**
Library of Congress – Conservation Division

WATER TYPE

Washing, general

Advantages

- Aqueous washing treatments improve the strength, flexibility, and brightness of paper
- Aqueous washing treatments remove iron (II) ions, acids, and other water-soluble degradation products

Disadvantages

- No aqueous washing treatment will prevent ink corrosion from re-occurring in documents that contain iron-gall ink. Additional treatment, such as complexing and alkalinization, is needed for long-term protection.
- May affect the appearance of the ink (fading, bleeding, sinking, color change, potential dissolving of ink binder)

Tap water

Advantages

- Readily available

Disadvantages

- The chemical composition of tap water varies. Tap water may require treatment to be suitable for conservation purposes.

Deionized water (~pH 6)

Advantages

- Metal ions, chlorine, and organic impurities are removed

Disadvantages

- Absence of all metal ions results in an aggressive washing solution that may remove beneficial ions from the paper and adversely affect its long-term stability
- Water quality varies over time. Monitoring the water produced by the deionizing system is recommended.
- Washing in this type of water may cause components of ink to bleed

Calcium hydroxide-adjusted deionized water (pH 7 – 8.5)

Advantages

- Calcium hydroxide ($Ca(OH)_2$) adjustment reduces the risk of removing beneficial ions from the paper
- Promotes removal of acidic degradation products from the ink and paper

Disadvantages

- If used in spray applications, calcium particles may clog the sprayer

Ammonium hydroxide-adjusted deionized water (pH 7 – 8.5)

Advantages

- Removes dirt and discoloration from paper more effectively than water alone or $Ca(OH)_2$-adjusted deionized water
- Can be used in spray applications without clogging the sprayer

Disadvantages

- May cause graying of paper
- May cause unwanted changes to colorants in paper
- The pH of the wash bath can be difficult to maintain as ammonium hydroxide (NH_4OH) is volatile and evaporates quickly
- Using NH_4OH requires additional precautions for health and safety

PROTOCOLS for IRON-GALL INK TREATMENT NOTES **FIG. 10**
Library of Congress – Conservation Division

WATER TEMPERATURE

Temperature of water (approximate)

	Fahrenheit	Celsius
"**Room**"	68ºF	20ºC
Tepid	80ºF	~27ºC
Warm	90ºF or >	~32ºC or >
Hot	120ºF or >	~49ºC or >
Simmering	<212ºF	<100ºC

Washing in all temperatures of water

Advantages

- Aqueous washing treatments improve the strength, brightness, and flexibility of the paper
- Aqueous washing treatments remove iron (II) ions, acids, and other water-soluble degradation products from the ink and paper

Disadvantages

- No aqueous washing treatments prevent ink corrosion from re-occurring in documents that contain iron-gall ink. Additional treatment, such as complexing and alkalinization, is needed for long-term protection.
- May affect the appearance of the ink (fading, bleeding, sinking, color change, potential dissolving of ink binder)

Increasing water temperature for washing

Advantages

- May improve the brightness of the paper
- May accelerate and enhance the removal of iron (II) ions, acids, degraded size, and other water-soluble degradation products from the ink and paper. May also shorten the duration of washing treatment.

Disadvantages

- May affect the appearance of the ink (fading, bleeding, sinking, color change, potential dissolving of ink binder)
- May cause color change in the paper, possibly over-whitening it or imparting a gray cast
- May increase swelling of paper fibers and cause visual changes to the ink and paper
- Higher temperatures may cause undesirable alteration or removal of sizing, colorants, and other components of paper manufacture

Simmering water treatment

Advantages

- Improves the brightness of the paper
- Very efficient at removing iron (II) ions, acids, degraded size, and other water-soluble degradation products from the ink and paper. Can significantly shorten the duration of washing treatment.
- May increase the flexibility of the paper

Disadvantages

- May affect the appearance of the ink (fading, bleeding, sinking, color change, potential dissolving of ink binder)
- May cause color change in the paper, possibly over-whitening it or imparting a gray cast
- May cause the paper to shrink
- May cause physical damage to ink-corroded paper (cracks, breaks, losses)
- Probability of unwanted changes occurring to ink and/or paper cannot be predicted through testing
- An aggressive treatment that has a limited application

SOURCES CONSULTED

Biggs, Julie L. 2006. The conservation of iron-gall ink on paper. *Working paper*. FAIC Samuel H. Kress Conservation Publication Fellowship.

PROTOCOLS for IRON-GALL INK TREATMENT NOTES **FIG. 11.1**
Library of Congress – Conservation Division

WASHING METHODS

Immersion (placing object in a bath of solution)

Advantages

- Unrestricted access of water to the object makes it an effective procedure for washing
- Easiest method of washing

Disadvantages

- Least controllable of the aqueous washing procedures

Suction table (spraying or misting object on suction table at low setting)

Advantages

- Less aggressive than immersion, so it is less likely to cause changes to the ink
- Restricts movement of the paper during treatment
- Allows control of the solution amount, location, and duration of application

Disadvantages

- Washing may be incomplete, leaving degradation products and iron ions in the paper (immersion is more likely to move the components out of the paper)
- May promote lateral migration of ions and degradation products within the paper
- Suction may cause sinking of ink
- Uneven drying, distortion, and dimensional changes in the paper are possible
- Preferable for one-sided documents

Screen washing (placing object on a screen in a bath of solution**)**

Advantages

- Provides support for the object while allowing complete contact between the solution and the paper

Disadvantages

- Requires careful monitoring to ensure effective washing

Fluxion, blotter, and other capillary washing

- Generally not recommended for iron-gall ink on paper as capillary action may cause unwanted movement of ink components

Increased number of applications (repeating procedure)

Advantages

- Fresh solutions encourage more effective washing
- Offers an alternative to increased duration of washing and may achieve similar results

Disadvantages

- Requires more solution

Increased duration of application (extending the length of time of the procedure)

Advantages

- May result in more effective removal of degradation products, iron ions, and acidic components

Disadvantages

- Difficult to replicate conditions of prolonged treatment when performing solubility tests

PROTOCOLS for IRON-GALL INK TREATMENT NOTES **FIG.11.2**
Library of Congress – Conservation Division

WASHING METHODS

Series of varied applications (combining different application methods for one object)

Advantages

- Allows for customized treatment to meet specific needs of the object

Disadvantages

- Requires more planning to execute effectively

Agitation (physically moving water across the surface, either overall or locally)

Advantages

- Periodic movement of water across the surface of the paper increases the transfer of degradation products from the paper into the bath
- Agitation above a discrete stain may remove chromophoric degradation products from that area

Disadvantages

- May lead to the loss or movement of ink into the bath as the water moves across the surface of the paper.

SOURCES CONSULTED

Biggs, Julie L. 2006. The conservation of iron-gall ink on paper. *Working paper*. FAIC Samuel H. Kress Conservation Publication Fellowship.

PROTOCOLS for IRON-GALL INK TREATMENT NOTES **FIG. 12**
Library of Congress – Conservation Division

ETHANOL-MODIFIED WASHING

Ethanol and water solutions, general

Advantages

- Allows for treatment of most/many water-soluble inks
- Inclusion of ethanol in the solution can restrict the expansion of the paper, which may be desirable for paper with extensive physical damage
- May reduce the solubility of the ink in water, allowing for subsequent treatments with successively greater amounts of water

Disadvantages

- Ink components may sink or migrate into the paper
- Using ethanol requires additional precautions for health and safety

50% ethanol and 50% water

Advantages

- Most often selected for slightly water-soluble inks
- May help prevent losses and cracking of the ink and splitting of the paper

Disadvantages

- Less effective than 100% water in removing discoloration and acidic components
- Repeated baths or additional treatment may be needed to remove iron (II) ions
- The pH of the paper may not rise as much as it would with water alone
- May affect ethanol-sensitive compounds present in the ink and paper (the probability for change may be predicted through careful testing)

66.6% ethanol and 33.3% water

Advantages

- For inks that are exceedingly soluble in water, this solution may still allow some of the benefits of washing

Disadvantages

- The comments made for the 50% ethanol and 50% water solution apply, but with greater emphasis

10% ethanol and 90% water

Advantages

- Inclusion of a small amount of ethanol to the washing solution may help to wet out papers that are heavily sized or that would wet out unevenly due to damage caused by ink corrosion, mold, or other factors

Disadvantages

- May affect ethanol-sensitive compounds present in the ink and paper. The probability for change may be predicted through careful testing.

PROTOCOLS for IRON-GALL INK TREATMENT NOTES **FIG. 13.1**
Library of Congress – Conservation Division

DRYING

Preliminary drying - Chemical

Ethanol immersion

Advantages

- Ethanol displaces water in paper, speeding drying while reducing contraction of paper
- Immersion ensures uniform saturation
- May reduce risk of bleeding of water-sensitive ink while drying

Disadvantages

- Not suitable for ethanol-sensitive inks
- Using ethanol requires additional precautions for health and safety

Ethanol spray

Advantages

- Ethanol displaces water in paper, speeding drying while reducing contraction of paper
- May reduce risk of bleeding of water-sensitive ink while drying
- Can be applied in smaller amounts than immersion and/or local application

Disadvantages

- Not suitable for ethanol-sensitive inks
- Using ethanol requires additional precautions for health and safety

Preliminary drying - Physical

Partial air drying (removing object from bath and placing briefly on blotter or drying screen to expose paper to air before complete drying. Complete air drying not recommended for iron-gall inks on paper.)

Advantages

- Water evaporates from object more slowly than by other methods but is dependent on the ambient temperature, relative humidity, or air circulation
- Less contact with ink surface than with blotter or suction table techniques

Disadvantages

- None

Blotting (placing object briefly between blotters to absorb excess moisture before complete drying)

Advantages

- Rapidly moves water away from paper surface

Disadvantages

- Contacts surface of ink, and is therefore not recommended for inks that are fragile or show transfer during testing. Can be mitigated by using a polyester web barrier.

Suction table (placing object on blotter on suction table to draw out excess moisture before complete drying)

Advantages

- Helps to limit lateral movement of soluble ink components
- Rapidly moves water away from the paper

Disadvantages

- May cause the ink to sink into the paper
- May flatten or disrupt ink topography
- May cause paper to dry unevenly or at expanded dimensions, imparting physical stress to ink-inscribed paper

PROTOCOLS for IRON-GALL INK TREATMENT NOTES **FIG. 13.2**
Library of Congress – Conservation Division

DRYING

Drying

Between blotters only

Advantages

- Rapidly moves water away from paper surface

Disadvantages

- Ink transfer to blotter may occur
- Ink topography may be disrupted by rough surface of blotter
- Blotter may adhere to object
- Transfer of any optical brighteners in blotter more likely without a polyester web barrier

Between polyester web and blotters

Advantages

- Rapidly moves water away from paper surface
- Polyester web may prevent ink transfer onto blotter
- Smooth polyester web allows an object to move as it dries

Disadvantages

- Certain types of polyester web may snag ink-corroded paper
- Dense polyester web may inhibit transfer of moisture from the surface and slow drying

Between polyester web and wool felts

Advantages

- Inhibits transfer of moisture and promotes slow drying

Disadvantages

- Inhibits transfer of moisture and promotes slow drying
- Certain types of polyester web may snag ink-corroded paper

Directional drying (between combinations of polyester web, blotters, felts, or barrier layers)

Advantages

- Absorbent and hydrophobic materials can be used in various combinations to direct or control drying to reduce the risk of sinking or other changes to the ink

Disadvantages

- Requires experience and practice to achieve the desired results

Suction table

Advantages

- Helps limit lateral movement (bleeding) of soluble ink components

Disadvantages

- May cause the ink to sink into the paper
- May flatten or disrupt ink topography
- May cause paper to dry unevenly or at expanded dimensions, imparting physical stress to ink-inscribed paper

Restraint

Overall, heavy weight (using a press, clamped system or heavy weights)

Advantages

- Allows close surface contact with paper and drying materials to promote quick transfer of moisture to drying materials

Disadvantages

- May flatten ink or paper topography
- May cause the sheet to dry at expanded dimensions, imparting physical stress to ink-inscribed paper

PROTOCOLS for IRON-GALL INK TREATMENT NOTES **FIG. 13.3**
Library of Congress – Conservation Division

DRYING

Overall, light weight (using acrylic sheet or glass sheet without additional weight)

Advantages

- Does not flatten ink or paper topography

Disadvantages

- May not provide adequate surface contact between paper and drying materials, causing uneven drying or distortion

Weight applied to edges

Advantages

- In conjunction with felts, can hold object in place without flattening the ink

Disadvantages

- May place uneven stresses on paper and/or ink

Stretch drying (tensioned drying of object)

Advantages

- Drying is rapid
- No contact with ink surface

Disadvantages

- May stretch paper beyond original dimensions, imparting physical stress to ink-inscribed paper
- Not recommended for physically compromised objects

PROTOCOLS for IRON-GALL INK TREATMENT NOTES **FIG. 14**
Library of Congress – Conservation Division

BOOKKEEPER® SPRAY SYSTEM

Bookkeeper® is a dispersion of sub-micron-sized particles of magnesium oxide in perfluoroalkane with a surfactant (a proprietary perfluoropolyether derivative).

Advantages

- Imparts a significant alkaline reserve to paper. (The manufacturer, Preservation Technologies, states that the final pH after treatment ranges from pH 7-10 and deposits 1.5% calcium carbonate by weight to paper.)
- Can be used on inks that are soluble in water and ethanol
- Can be used on objects that cannot be treated with aqueous or ethanol-modified aqueous solutions

Disadvantages

- Does not remove acids or other water-soluble degradation products from the ink and paper
- The effect of Bookkeeper® on iron-gall ink has not been extensively analyzed
- Uneven deposition may occur
- May leave a fine powdery residue on the ink and paper
- Using Bookkeeper® requires additional precautions for health and safety

SOURCES CONSULTED

Boone, Terry, Lynn Kidder, and Susan Russick. 1998. Bookkeeper® for spray use in single item treatments. *AIC Book and Paper Group Annual*, 17:29-43.

Stauderman, Sarah D., Irene Brückle, and Judith J. Bischoff. 1996. Observations on the use of Bookkeeper® Deacidification Spray for the treatment of individual objects. *AIC Book and Paper Group Annual*, 15:11-19.

PROTOCOLS for IRON-GALL INK TREATMENT NOTES **FIG. 15.1**
Library of Congress – Conservation Division

CALCIUM BICARBONATE

Advantages

- Provides an alternative treatment for ink and/or paper that is sensitive to alkaline pH and that may be visually altered by a magnesium-based alkaline treatment
- Can remove water-soluble acids from paper more effectively than washing alone
- Research conducted at the Library of Congress indicated that calcium bicarbonate treatment is effective according to the following criteria:
  - pH, alkaline reserve
    - Compared to no treatment or to washing only, resulted in a small increase of surface pH of inked and non-inked regions of sized rag paper
    - Provided some alkaline reserve
  - Paper brightness
    - Compared to no treatment or to washing only, resulted in a subtle increase in brightness of unsized and sized rag paper after artificial aging
  - Ink color
    - Did not significantly alter the color of the ink, consistent with other calcium-based treatments

Disadvantages

- Preparation of treatment solution is time-consuming. Advance chilling of water is necessary.
- Preparation requires additional precautions for health and safety
- Solution best used immediately after preparation. Storage requires airtight container and cool temperature.
- Research conducted at the Library of Congress indicated that calcium bicarbonate has drawbacks according to the following criteria:
  - pH, alkaline reserve
    - Low concentration of alkaline salts and small buffering capacity provide limited protection against future degradation of ink and paper
  - Burst testing
    Compared to magnesium bicarbonate treatment, or calcium phytate with calcium bicarbonate, is less effective at preserving paper strength and elasticity

PROTOCOLS for IRON-GALL INK TREATMENT NOTES **FIG. 15.2**
Library of Congress – Conservation Division

CALCIUM BICARBONATE

Preparation of calcium bicarbonate solution using compressed carbon dioxide (CO_2) gas

This method, modifying that of the Netherlands Institute for Cultural Heritage, was developed by the LC Iron-Gall Ink Corrosion Group in 2004.

volume of calcium bicarbonate solution produced	**100 ml**	**500 ml**	**1 liter**	**4 liters**	**10 liters**	**40 liters**
calcium carbonate, powdered	0.11 gm	0.55 gm	1.1 gm	4.4 gm	11 gm	44 gm
deionized water, chilled overnight	100 ml	500 ml	1 liter	4 liters	10 liters	40 liters
carbon dioxide gas	as needed					

- Fill container with chilled deionized water to the required amount
- Place container on a stirring plate with a stirring bar in center of base of container
- Attach a light weight to gas diffuser or nozzle to hold it near the base of the container for maximum dispersion of CO_2 gas
- Turn on stirrer. Adjust the speed as needed to produce rapid movement of the solution.
- Turn on gas. Adjust flow rate to produce vigorous bubbling of CO_2 gas through the solution.
- Add calcium carbonate powder gradually. Adjust stir rate and/or flow rate to prevent settling of the powder, as settled powder will not go into solution.
- Bubble CO_2 gas through mixture until the powder is dissolved. In a covered, unpressurized container, 10 liters may take up to 3 to 4 hours to make. Check the solution periodically to make sure the stirrer position remains at the center of the base of the container and that there is sufficient CO_2 gas in the tank.
- Solution is ready when all or nearly all the calcium bicarbonate powder is dissolved. Decanting may be necessary.
- To avoid formation of a gritty residue on trays or in spray nozzles, clean equipment immediately after use

The pH of the solution should be 5.8 to 5.9. The solution is most effective when used immediately after preparation, otherwise the equilibrium of the solution shifts as CO_2 diffuses out of it and the calcium bicarbonate precipitates out as calcium salts. If it is necessary to store the solution, an airtight container at cool temperature is recommended. Re-bubble with CO_2 gas before use if required.

Treatment

- Pour solution into tray
- Immerse the object in the solution and cover the surface with polyester film. Place the film directly in contact with the solution to slow the diffusion of CO_2 and the precipitation of calcium salts.
- After 20-30 minutes of immersion, remove the object and partially dry on a blotter
- Air dry the object briefly, then place it between felts and/or blotters to dry and flatten

Sources consulted

Biggs, Julie L. 2006. The conservation of iron-gall ink on paper. *Working paper*. FAIC Samuel H. Kress Conservation Publication Fellowship.

Connelly-Ryan, Cindy, et al. 2007. Optimizing ink corrosion treatment protocols at the Library of Congress. In *Edinburgh Conference Papers 2006*, ed. Shulla Jaques. London: Institute of Conservation, 195-202.

PROTOCOLS for IRON-GALL INK TREATMENT NOTES **FIG. 16.1**
Library of Congress – Conservation Division

CALCIUM PHYTATE / CALCIUM BICARBONATE TREATMENT

Advantages

- Calcium phytate complexes, or binds, iron (II) ions in corroded inks to inhibit further corrosion. Calcium bicarbonate aids in the removal of water-soluble acidic degradation products and may deposit a small quantity of alkaline reserve in the paper.
- Provides an alternative treatment option for ink and paper that may be visually altered (ink color may shift) by magnesium-based alkaline treatments
- May be appropriate as a single aqueous treatment for extremely corroded ink and deteriorated paper that can sustain only brief treatment, i.e., the washing treatment is eliminated
- May result in increased brightness of the paper
- Research conducted at the Library of Congress indicated that calcium phytate/ calcium bicarbonate is effective according to the following criteria:
  - pH, alkaline reserve
    - Resulted in a smaller increase in pH of paper as compared to magnesium-based alkaline treatments
    - pH was higher than for both untreated and washed samples
    - After artificial aging, pH was higher than the untreated, washed, and calcium bicarbonate-only treated samples
    - Provided a higher alkaline reserve than calcium bicarbonate alone
  - Burst Testing
    - Rag papers treated with calcium phytate/calcium bicarbonate demonstrated a high peak load (tensile or breaking strength), degree of elongation (fiber stretch), and burst energy absorption (tensile energy absorption), comparable to papers treated with magnesium bicarbonate solutions
  - Iron (II) ion Testing
    - Most effective in preventing regeneration of iron (II) ions in unsized paper, and was as effective as other phytate protocols for sized papers
  - Paper Brightness
    - Remained the brightest in tone after artificial aging compared to other treatment methods
  - Ink Color
    - Did not significantly alter the color of the ink

Disadvantages

- Preparation of treatment solutions is a time-consuming, two-step process
- Preparation, use, and disposal require additional precautions for health and safety
- White phytate salt deposits may form on the surface of the ink and paper after drying
- May result in an undesirable degree of brightening of the paper

Preparation of calcium phytate solution

Calcium phytate treatment involves two separate treatment steps:

(1) Calcium phytate treatment
(2) Calcium bicarbonate treatment

Calcium bicarbonate is required to make the calcium phytate solution and the alkaline treatment solution. Begin by determining the amount of solution needed for treating the object(s). The amount will depend on the size of tray required for immersion or other application. Ensure that there is enough calcium bicarbonate solution for both treatment steps.

Preparing calcium phytate requires the storage and handling of phytic acid (myo inositol hexakisphosphate, frequently supplied as inositol hexaphosphoric acid). The treatment solution is acidic. Conservators should wear protective clothing: lab coat or equivalent, appropriate gloves, and eye protection.

Check the label to ensure that the phytic acid is within its shelf life (3 years from the date of opening). If opening the bottle for the first time, clearly mark the date on the label. Phytic acid is a clear or pale-yellow to amber color; if it is dark brown and/or contains solids, it should not be used.

PROTOCOLS for IRON-GALL INK TREATMENT NOTES **FIG. 16. 2**
Library of Congress – Conservation Division

CALCIUM PHYTATE / CALCIUM BICARBONATE TREATMENT

volume of calcium phytate solution produced	**250 ml**	**500 ml**	**1 liter**	**10 liters**	**20 liters**
1. phytic acid solution, 40% *or* 2. phytic acid solution, 50%	0.72 gm 0.57 gm	1.44 gm 1.14 gm	2.88 gm 2.28 gm	28.8 gm 22.8 gm	57.6 g 45.6 gm
calcium bicarbonate solution	100 ml	200 ml	400 ml	4 liters	8 liters
deionized water	max. 250 ml	max. 500 ml	max. 1 liter	max. 10 liters	max. 20 liters
ammonium hydroxide, 3%	ca. 2 ml	ca. 5 ml	ca. 10 ml	ca. 100 ml	ca. 200 ml

Instructions are for a total volume of 1 liter calcium phytate
Using the table above, modify the instructions for the volume of calcium phytate solution needed

- Work in a chemical hood
- Check the label to see if the phytic acid solution is 40% or 50% and choose the appropriate amount from the table above
- Pour a few milliliters (ml) of concentrated phytic acid solution from the original bottle into a beaker.
- Using a glass pipette, transfer the needed weight (in grams) of solution into another beaker.
- Dilute the phytic acid with about 50 ml deionized water and pour the solution into a beaker with a volume of at least 1 liter
- While stirring, add 400 ml of calcium bicarbonate solution. Calcium bicarbonate should be prepared according to the instructions entitled “Calcium Bicarbonate.”
- Fill with deionized water to a total volume of 950 ml. If making more than 1 liter, ensure that the mixing container can accommodate the addition of ammonium hydroxide, which may exceed the approximate amounts given in the table above.
- While stirring the liquid, gradually add ammonium hydroxide with a pipette until the solution turns slightly turbid (approximately 10 ml). Dark colored paper or card may be placed behind the beaker to observe the change to the solution. Check the pH, which should have reached a value of 5.5-6.0.
- Fill up the container with deionized water to a total volume of 1 liter. Ensure that the pH is still 5.5-6.0.

The solution has an approximate concentration of 1.75 mmol/l calcium phytate, equivalent to 0.116% phytic acid. The solution is most effective when used immediately after preparation. Calcium phytate solution can spoil if it is kept for an extended period. In addition, the equilibrium of the solution shifts as carbon dioxide (CO_2) diffuses out of it, causing calcium salts to precipitate.

If storing is necessary, prepare the calcium phytate but do not add ammonium hydroxide until immediately prior to use. Calcium phytate should be refrigerated in an airtight container for no longer than 48 hours.

PROTOCOLS for IRON-GALL INK TREATMENT NOTES **FIG. 16.3**
Library of Congress – Conservation Division

CALCIUM PHYTATE / CALCIUM BICARBONATE TREATMENT

Treatment

Step 1

- Pour calcium phytate solution into tray
- Immediately immerse the object in the solution and cover the surface with polyester film. Place the film directly in contact with the solution to slow diffusion of CO_2 and precipitation of calcium salts
- After 20 minutes immersion, remove the object and blot excess treatment solution

Step 2

- Pour calcium bicarbonate solution into tray
- Immerse the object in the solution and cover the surface with polyester film. Place the film directly in contact with the solution to slow diffusion of CO_2 and precipitation of calcium salts.
- After 20-30 minutes immersion, remove the object and partially dry on a blotter
- Air dry the object briefly, then place it between felts and/or blotters to dry and flatten
- Waste solutions of calcium phytate or calcium bicarbonate that contain no ethanol may be disposed of in the sink

SOURCES CONSULTED

Biggs, Julie L. 2006. The conservation of iron-gall ink on paper. Working paper. FAIC Samuel H. Kress Conservation Publication Fellowship.

Connelly-Ryan, Cindy, et al. 2007. Optimizing ink corrosion treatment protocols at the Library of Congress. In *Edinburgh Conference Papers 2006*, ed. Shulla Jaques. London: Institute of Conservation, 195-202.

PROTOCOLS for IRON-GALL INK TREATMENT NOTES **FIG. 17.1**
Library of Congress – Conservation Division

ETHANOL-MODIFIED CALCIUM PHYTATE / CALCIUM BICARBONATE TREATMENT

Advantages

- Ethanol-modified calcium phytate complexes, or binds, iron (II) ions in water-soluble corroded inks to inhibit further corrosion. Ethanol-modified calcium bicarbonate aids in the partial removal of acidic degradation products and may deposit a small quantity of alkaline reserve in the paper.
- Provides an alternative treatment option for ink and paper that may be visually altered (ink color may shift) by a magnesium-based alkaline treatment
- May be appropriate as a single aqueous treatment for extremely corroded ink and deteriorated paper that can sustain only brief treatment (i.e., the washing treatment is eliminated)
- May result in increased brightness of the paper

Disadvantages

- Preparation of treatment solutions is a time-consuming, two-step process. Advance chilling of solutions is necessary.
- Preparation, use, and disposal requires additional precautions for health and safety
- White phytate salt deposits may form on the surface of the ink and paper after drying
- Addition of ethanol to aqueous calcium phytate and calcium bicarbonate dilutes the solutions and results in some precipitation of salts, which may reduce the efficacy of the treatment. The long-term efficacy has not been extensively studied.

Preparation of calcium phytate solution

Ethanol-modified calcium phytate treatment involves two separate treatment steps:

(1) Ethanol-modified calcium phytate treatment
(2) Ethanol-modified calcium bicarbonate treatment

Making ethanol-modified calcium phytate and calcium bicarbonate solutions requires the preparation of aqueous calcium phytate and calcium bicarbonate solutions to which ethanol is then added.

Calcium bicarbonate is required for the calcium phytate solution and the alkaline treatment solution. Begin by determining the amount of solution needed for treating the object(s). The amount will depend on the size of tray required for immersion or other method of treatment application. Take into account that the solutions will be diluted with a proportion of ethanol. Ensure that there is enough calcium bicarbonate for both treatment steps.

Preparing calcium phytate requires the storage and handling of phytic acid
(myo inositol hexakisphosphate; frequently supplied as inositol hexaphosphoric acid).
The treatment solution is also acidic. Conservators should wear protective clothing: lab coat or equivalent, appropriate gloves, and eye protection.

Check the label to ensure that the phytic acid is within its shelf life (3 years from the date of opening). If opening the bottle for the first time, clearly mark the date on the label. The solution should be a clear or pale-yellow to amber color; if it is dark brown and/or contains solids, it should not be used.

PROTOCOLS for IRON-GALL INK TREATMENT NOTES **FIG. 17.2**
Library of Congress – Conservation Division

ETHANOL-MODIFIED CALCIUM PHYTATE / CALCIUM BICARBONATE TREATMENT

volume of calcium phytate solution produced	**250 ml**	**500 ml**	**1 liter**	**10 liters**	**20 liters**
1. phytic acid solution, 40% *or* 2. phytic acid solution, 50%	0.72 gm 0.57 gm	1.44 gm 1.14 gm	2.88 gm 2.28 gm	28.8 gm 22.8 gm	57.6 gm 45.6 gm
calcium bicarbonate solution	100 ml	200 ml	400 ml	4 liters	8 liters
deionized water	max. 250 ml	max. 500 ml	max. 1 liter	max. 10 liters	max. 20 liters
ammonium hydroxide, 3%	ca. 2 ml	ca. 5 ml	ca. 10 ml	ca. 100 ml	ca. 200 ml

Instructions are for a total volume of 1 liter calcium phytate
Using the table above, modify the instructions for the volume of calcium phytate solution needed

- Work in a chemical hood
- Check the label to see if the phytic acid solution is 40% or 50% and choose the appropriate amount from the table above
- Pour a few milliliters (ml) of concentrated phytic acid solution from the original bottle into a beaker. Using a glass pipette, transfer the needed weight (in grams) of solution into another beaker.
- Dilute the phytic acid with about 50 ml deionized water and pour the solution into a beaker with a volume of at least 1 liter
- While stirring, add 400 ml of calcium bicarbonate solution. Calcium bicarbonate should be prepared according to the instructions entitled “Calcium Bicarbonate”
- Fill with deionized water to a total volume of 950 ml. If making more than 1 liter, ensure that the mixing container can accommodate the addition of ammonium hydroxide, which may exceed the approximate amounts given in the table above.
- While stirring the liquid, gradually add ammonium hydroxide with a pipette until the solution turns slightly turbid (approximately 10 ml). Dark colored paper or card may be placed behind the beaker to observe the change to the solution. Check the pH, which should have reached a value of 5.5-6.0.
- Fill with deionized water to a total volume of 1 liter. Ensure that the pH is still 5.5-6.0.

The solution has an approximate concentration of 1.75 mmol/l calcium phytate, equivalent to 0.116% phytic acid. The solution is most effective when used immediately after preparation. Calcium phytate solution can spoil if it is kept for an extended period. In addition, the equilibrium of the solution shifts as CO_2 diffuses out of it causing calcium salts to precipitate.

If storing is necessary, prepare the calcium phytate but do not add the ammonium hydroxide until immediately prior to use. Calcium phytate should be refrigerated in an airtight container for no longer than 48 hours.

PROTOCOLS for IRON-GALL INK TREATMENT NOTES **FIG. 17. 3**
Library of Congress – Conservation Division

ETHANOL-MODIFIED CALCIUM PHYTATE / CALCIUM BICARBONATE TREATMENT

Preparation of ethanol-modified calcium phytate and ethanol-modified calcium bicarbonate solutions

Common proportion options are:

25% ethanol / 75% calcium phytate and 25% ethanol / 75% calcium bicarbonate
33% ethanol / 66% calcium phytate and 33% ethanol / 66% calcium bicarbonate
50% ethanol / 50% calcium phytate and 50% ethanol / 50% calcium bicarbonate

NOTE: **Do not use more than 50% ethanol with each solution.**
The Netherlands Institute for Cultural Heritage recommends using solutions with no more than 50% ethanol. The addition of ethanol will reduce the efficacy of the aqueous solutions and causes the precipitation of calcium salts.

- Work in a chemical hood
- Wear labcoat, appropriate gloves, and approved eye protection
- Measure the ethanol needed for each of the two steps. Refrigerate overnight in a labeled, airtight container.
- Immediately before beginning the complexing treatment, add the ethanol to the calcium phytate and mix well
- Immediately before beginning the alkaline treatment, add the ethanol to the calcium bicarbonate and mix well

Treatment

Step 1

- Pour ethanol-modified calcium phytate solution into tray
- Immerse the object in the solution and cover the surface of the solution with polyester film. Place the film directly in contact with the surface of the solution to slow diffusion of CO_2 and precipitation of calcium salts.
- After 20 minutes immersion, remove the object and partially dry on a blotter

Step 2

- Pour ethanol-modified calcium bicarbonate solution into tray
- Immerse the artifact in the solution and cover the surface of the solution with polyester film. Place the film directly in contact with the surface of the solution to slow diffusion of CO_2 and precipitation of calcium salts.
- After 20-30 minutes immersion, remove the object and partially dry on a blotter
- Air dry the object briefly, then place it between felts and/or blotters to dry and flatten

SOURCES CONSULTED

Biggs, Julie L. 2006. The conservation of iron-gall ink on paper. Working paper. FAIC Samuel H. Kress Conservation Publication Fellowship.

PROTOCOLS for IRON-GALL INK TREATMENT NOTES **FIG. 18.1**
Library of Congress – Conservation Division

MAGNESIUM BICARBONATE

Advantages

- Has undergone extensive analytical testing and has been observed to perform well over time
- Imparts a significant alkaline reserve to paper
- Research conducted at the Library of Congress indicated that magnesium bicarbonate is effective according to the following criteria:
  - pH, alkaline reserve
    - Elevated pH of both inked and non-inked areas
    - Imparted a higher alkaline reserve than for calcium-based alkaline treatments
  - Burst testing
    - Rag papers treated with magnesium bicarbonate demonstrated a high peak load (tensile or breaking strength), degree of elongation (fiber stretch), and burst energy absorption (tensile energy absorption), comparable to papers treated with phytate solutions
  - Iron (II) ion testing
    - Was effective in slowing the regeneration of iron (II) ions
  - Paper brightness
    - Retained brightness in comparison to untreated samples
  - Paper color
    - Pronounced yellowing of magnesium-treated papers seen in other studies not observed in rag papers

Disadvantages

- Preparation of treatment solution is time-consuming. Advanced chilling of water is necessary.
- Preparation requires additional precautions for health and safety
- May cause color shift in inks and pigmented seals.
- Research conducted at The Library of Congress indicated that magnesium bicarbonate has drawbacks according to the following criteria:
  - pH, alkaline reserve
    - pH may increase over time
  - Burst testing
    - Unsized sulfite papers demonstrated a lower peak load, elongation to break, and burst energy absorption than rag papers
  - Ink color
    - Can cause red shift in ink color, typical of treatments with magnesium compounds

PROTOCOLS for IRON-GALL INK TREATMENT NOTES **FIG. 18.2**
Library of Congress – Conservation Division

MAGNESIUM BICARBONATE

Preparation of magnesium bicarbonate solution using compressed carbon dioxide (CO_2) gas

The Conservation Division generally makes a 0.10M stock solution with magnesium hydroxide powder. The stock solution is diluted for use. Magnesium carbonate powder may also be used for the stock solution, but it requires a different measured amount and takes longer to go into solution.

volume of 0.10 M magnesium bicarbonate solution produced	**1 liter**	**14 liters**
1. magnesium hydroxide powder *or* 2. magnesium carbonate powder	5.7 gm 8.5 gm	80 gm 119 gm
deionized water, chilled	1 liter	14 liters
carbon dioxide gas	as needed	

- Fill container with chilled deionized water to the required amount
- Place container on a stirring plate and a stirring bar in center of base of container
- Attach a light weight to gas diffuser or nozzle to hold it near the base of the container for maximum dispersion of CO_2 gas
- Turn on stirrer. Adjust the speed as needed to produce rapid movement of the solution.
- Turn on gas. Adjust flow rate to produce vigorous bubbling of CO_2 gas through the solution.
- Bubble CO_2 gas through the mixture until the powder is dissolved. In an unpressurized container, 14 liters may take up to 3 hours to make. Check the solution periodically to make sure the stirrer position remains at the center of the base of the container and that there is sufficient CO_2 gas in the tank.
- After the powder has dissolved, allow the solution to settle for several hours before measuring the amount of effective carbonate in it, either by titration or by a proprietary method, such as the Taylor Hardness Kit

Treatment

- If the 0.10 M stock solution is not clear, filter before use
- Dilute the solution to 1 part magnesium bicarbonate to 4 parts deionized water. A more dilute solution may be desirable for a very lightweight paper.
- After 20-30 minutes immersion, remove document and partially dry on blotter
- Air dry briefly and place between felts and/or blotters to dry and flatten
- To avoid formation of a gritty residue on trays or in spray nozzles, clean equipment immediately after use

SOURCES CONSULTED

Biggs, Julie L. 2006. The conservation of iron-gall ink on paper. Working paper. FAIC Samuel H. Kress Conservation Publication Fellowship.

Krueger, Holly. 2004. Magnesium reconsidered. *AIC Book and Paper Group Annual*, 22:33-39.

The deacidification and alkalization of documents with magnesium bicarbonate. 1978. *Library of Congress publications on conservation of library materials: conservation workshop notes on evolving procedures,* Series 500., no. 1. Working Draft (July).

Wilson, William K., Mary C. McKiel, James Gear, and Robert H. MacClaren. 1979. *Preparation of solutions of magnesium bicarbonate for deacidification of documents*. Washington, DC: Preservation Services Laboratory Preservation Services Division National Archives of the United States.

Connelly-Ryan, Cindy, et al. 2007. Optimizing ink corrosion treatment protocols at the Library of Congress. In *Edinburgh Conference Papers 2006*, ed. Shulla Jaques. London: Institute of Conservation, 195-202.

PROTOCOLS for IRON-GALL INK TREATMENT NOTES **FIG. 19.1**
Library of Congress – Conservation Division

ETHANOL-MODIFIED MAGNESIUM BICARBONATE

Advantages

- Imparts a significant alkaline reserve to paper
- Appropriate for inks that can sustain only brief or partially aqueous treatment
- Research conducted at the Library of Congress indicated that ethanol-modified magnesium bicarbonate (65% ethanol /10% water and 25% magnesium bicarbonate) is effective according to the following criteria:
  - pH, alkaline reserve
    - Elevated pH of inked and non-inked areas
    - Imparted a higher alkaline reserve than calcium-based alkaline treatments
    - Solutions absorbed more readily by sulfite and softwood papers than other aqueous alkaline treatments
  - Burst testing
    - Rag papers treated with ethanol-modified magnesium bicarbonate demonstrated a high peak load (tensile or breaking strength), degree of elongation (fiber stretch), and burst energy absorption (tensile energy absorption) comparable to papers treated with phytate solutions
  - Iron (II) ion testing
    - Was as effective as fully aqueous magnesium bicarbonate in slowing the regeneration of iron (II) ions
  - Paper brightness
    - Retained brightness in comparison to untreated samples
  - Paper color
    - Pronounced yellowing of magnesium-treated items seen in other studies not observed in rag or sulfite papers

Disadvantages

- Preparation of solution is time-consuming. Advance chilling of ethanol and water is necessary.
- Preparation, use, and disposal requires additional precautions for health and safety
- May cause color shift in inks and pigmented seals
- Not recommended for treating ligneous papers as magnesium bicarbonate can cause color change in the paper
- Research conducted at the Library of Congress indicated that ethanol-modified magnesium bicarbonate has drawbacks according to the following criteria:
  - Burst testing
    - Unsized rag and unsized sulfite papers demonstrated a lower peak load, degree of elongation, and burst energy absorption than rag papers
  - Ink color
    - Can cause a red shift in ink color, typical of treatments with magnesium compounds

PROTOCOLS for IRON-GALL INK TREATMENT NOTES **FIG. 19.2**
Library of Congress – Conservation Division

ETHANOL-MODIFIED MAGNESIUM BICARBONATE

Preparation of ethanol-modified magnesium bicarbonate solutions

Proportion options include:

65% ethanol / 10% water and 25% magnesium bicarbonate
50% ethanol / 25% water and 25% magnesium bicarbonate

Preparation of 65% ethanol / 10% water and 25% magnesium bicarbonate solution

- Work in a chemical hood
- Wear labcoat, appropriate gloves, and approved eye protection
- Measure ethanol and water needed and combine in a container. Refrigerate overnight in a labeled, airtight container.
- Place stirring bar at center of base of container and place container on stirring plate
- Attach a light weight to gas diffuser or nozzle to hold it near the base of the container for maximum dispersion of gas
- Turn on stirrer. Adjust the speed as needed to produce rapid movement of the solution.
- Turn on gas. Adjust flow rate to produce vigorous bubbling of gas through the solution.
- Cover the container to trap the CO_2
- Bubble carbon dioxide (CO_2) gas through solution for 20 minutes
- Slowly add the magnesium bicarbonate into the ethanol-water solution while the CO_2 gas is bubbled through
- Continue to bubble the CO_2 gas through the solution for 10-15 minutes or until solution is clear

Preparation of 50% ethanol / 25% water and 25% magnesium bicarbonate solution

- Work in a chemical hood
- Wear labcoat, appropriate gloves, and approved eye protection
- Measure the ethanol and deionized water needed. Combine and refrigerate overnight in a labeled, airtight container.
- Immediately before beginning the alkaline treatment, add the magnesium bicarbonate to the chilled ethanol-water solution and mix well

Treatment

- Pour the ethanol-modified magnesium bicarbonate solution into a tray
- Immerse the object in the solution and cover with polyester film. Place the film directly in contact with the surface to slow diffusion of CO_2 and precipitation of magnesium salts.
- After immersion for 20-30 minutes, remove the object and partially dry on a blotter
- Air dry the object briefly, then place it between felts and/or blotters to dry and flatten

SOURCES CONSULTED

Connelly-Ryan, Cindy, et al. 2007. Optimizing ink corrosion treatment protocols at the Library of Congress. In *Edinburgh Conference Papers 2006*, ed. Shulla Jaques. London: Institute of Conservation, 195-202.

PROTOCOLS for IRON-GALL INK TREATMENT NOTES **FIG. 20.1**
Library of Congress – Conservation Division

SIZING

Proteinaceous sizes

Gelatin size

Advantages

- Has undergone extensive analytical testing and has been observed to perform well over time
- Improves mechanical strength of paper
- Improves water and abrasion resistance of paper
- May protect paper against fluctuations of humidity
- May offer some protection against iron-gall ink corrosion by binding transition metal ions
- May protect the paper and the ink against degradation caused by oxidation
- Similar to the original size historically used in the production of most Western handmade papers

Disadvantages

- In poor environmental conditions, gelatin-sized paper may be vulnerable to mold or insect attack
- May yellow, either through overheating during use or in natural aging
- Modification of solution or application method may be necessary for water-sensitive inks

Preparation and application of gelatin size

The Conservation Division generally uses 0.25%-2% aqueous solutions of laboratory grade gelatin powder (e.g. Fisher 275 Bloom). The percentage of the solution is determined by the thickness and porosity of the paper as well as by the sizing retained by the paper after treatment. A more dilute solution may be appropriate for more porous papers.

The solution is expressed as weight to volume, e.g. 1% is 1 gm gelatin powder per 100 ml water

- Measure the quantities of gelatin powder and deionized water needed
- Heat the water and slowly add the powder to it
- After the gelatin has dissolved, allow solution to cool slightly before applying to the object. Solution may be applied by brushing onto the object through polyester web or by immersing the object in it.
- Blot the object with a blotter, change the polyester web and dry the object between felts and/or blotters

Aqueous gelatin solution may be modified with ethanol for water-sensitive inks

Parchment size

Advantages

- Provides protective properties similar to gelatin
- Similar to the original size historically used in the production of most Western handmade papers

Disadvantages

- The origin and purity of parchment clippings varies widely. Determination of the precise origin and composition of clippings is recommended.
- In poor environmental conditions, parchment-sized paper may be vulnerable to mold or insect attack

The Conservation Division generally does not apply parchment size to iron-gall ink-inscribed paper because the degree of polymerization of the size cannot be determined quantitatively.

PROTOCOLS for IRON-GALL INK TREATMENT NOTES **FIG. 20.2**
Library of Congress – Conservation Division

SIZING

Cellulose ether sizes

Methyl cellulose size

Advantages

- Prepared solutions have a longer shelf life than proteinaceous sizes
- Less vulnerable than proteinaceous sizing to mold or insect attack

Disadvantages

- At lower concentrations, does not improve mechanical strength of paper to the same degree as gelatin

Preparation and application of methyl cellulose size

The Conservation Division generally uses 0.5%-1% aqueous solutions of low molecular weight, short polymer length powdered methyl cellulose (e.g. Dow Methocel™A15C) for sizing.

- Measure the quantities of methyl cellulose powder and de-ionized water needed for solution
- Chill two thirds of the water and reserve
- Heat one third of the water to just under the boiling point
- Add the methyl cellulose powder to the heated water, whisking the mixture to disperse the powder
- Allow the solution to cool to room temperature for several hours, until sufficiently thickened. (See product container for suggestions of manufacturer or supplier.)
- Add the chilled water to the thickened solution
- Brush the solution onto the object through polyester web
- Blot the object with a blotter, change the polyester web and dry the object between felts and/or blotters

Aqueous methyl cellulose solution may be modified with ethanol for water-sensitive inks

Hydroxypropyl cellulose size

Advantages

- Can be dissolved in ethanol for application to water-sensitive inks

Disadvantages

- Does not improve mechanical strength of paper to the same degree as gelatin
- Use of ethanol requires additional precautions for health and safety

Preparation and application of hydroxypropyl cellulose size

The Conservation Division generally uses 1%- 2% solutions of hydroxypropyl cellulose (e.g. Klucel G® / Klucel GF®) in ethanol for sizing.

- Measure the quantities of hydroxypropyl cellulose powder and ethanol needed for solution
- Working in a chemical hood, heat the ethanol on a hot plate
- Add the hydroxypropyl cellulose powder to the warm ethanol, whisking the mixture to disperse the powder
- Cover the solution and allow it to cool to room temperature
- Brush the solution onto the object through polyester web
- Blot the object with a blotter, change the polyester web and dry the object between felts and/or blotters

SOURCES CONSULTED

Baker, Cathleen. 1985. Seminar on paper sizing. Presented at the AIC Annual Meeting, Washington.

Garlick, Karen. 1986. A brief review of the history of sizing and resizing practices. *AIC Book and Paper Group Annual*, 5:94-107.

Kolbe, Gesa. 2004. Gelatin in historical paper production and as inhibiting agent for iron-gall ink corrosion on paper. *Restaurator* 25 (1): 26-39.

Vitale, Timothy, et al. 1988. Sizing/resizing. *Paper Conservation Catalog*. 5th ed. Washington: American Institute for Conservation Book and Paper Group.