
Effect of Aqueous Treatments on Nineteenth-Century Iron-Gall-Ink Documents: Calcium Phytate Treatment—Optimization of Existing Protocols

ABSTRACT

Research results presented in this study were obtained in a project carried out at the Gatineau Preservation Centre, Library and Archives Canada (LAC) in partnership with the Canadian Conservation Institute (CCI) in Ottawa, Canada. This project uses nine original iron gall ink documents and compares various treatments with the combination of calcium phytate and calcium bicarbonate. The aim of this study was to identify visual changes, determine immediate side effects, and assess the effectiveness of delaying ink corrosion. Best results, which include an effective delay of ink corrosion and an alkaline reserve deposit, were achieved by immersing the naturally aged samples with a combined calcium phytate/calcium bicarbonate treatment. The significance of the findings is discussed.

INTRODUCTION

Thirteen years after the introduction of the aqueous calcium phytate treatment for ink-corroded materials proposed by the Instituut Collectie Nederland (ICN), this method is applied increasingly in paper conservation laboratories all over the world. For years paper and book conservators have been considering the recently developed treatments using calcium or magnesium phytate solutions with or without ethanol in addition to an alkaline reserve. Part 1 of this research includes: aqueous treatments; testing for solubility of corroded inks; measuring water absorption of the papers; measuring surface pH of inked areas; measuring cold water extraction pH; microchemical testing for detection of iron (II) ions with a bathophenanthroline paper indicator developed by Dr. Han Neevel (Reissland and de Groot 1999; Neevel and Reissland 2001; Eusman 2002); using a calibrated color chart developed by the Canadian Conservation Institute (CCI) (Tse et al. 2006); and evaluating the side effects (under magnification,

daylight, and ultraviolet fluorescence illuminations) using instrumental analyses and evaluation by test panels of conservators. Part 2 investigates the changes that occur in selected treated samples following artificial aging by exposure to heat, light, and humidity (Tse et al. 2006; Tse et al. 2010). These tests were carried out to address concerns regarding the sensitivity of media treated with phytate (Neevel and Reissland 1997), and the possibility of fungal growth when exposed to a high humidity environment (Homolka 2001).

EXPERIMENTAL

This research focused on the comparative effectiveness of currently used and newly developed aqueous treatments.¹

Samples

Nine original Canadian documents dating from the mid-nineteenth century (c. 1841–1875) were washed with eighteen separate aqueous treatments. The naturally aged ledgers were provided by CCI from their sample collection. The samples had different ink compositions and paper substrates and were selected for the study even though they were in relatively good condition overall, at the initial stages of ink corrosion (table 1). These documents were assessed to be in ICN condition rating 1 (Reissland and Hofenk de Graaff 2000).

The ledgers were cut into strips of various dimensions and one strip of each document was left untreated as a control sample. Some sets of samples did not receive all the proposed treatments due to the amount of sample material available.

Treatments Protocols

The individual sequences of wash combinations used are summarized in table 2.1 and 2.2. Samples were treated separately. Consequently, the solutions were individually prepared and performed without drying the samples in between. To ensure a standardized washing procedure, the nine sample sets and each aqueous treatment option were treated consistently (table 2.2 and fig. 1). Samples in this study were not

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Samples	Substrates	Media
1	1856 Cream wove paper; cotton rag; machine made; and with ruled lines	Dark brown ink ICN rating: 1 CCI Fe ²⁺ : 50+ ;Fe ³⁺ :50+
2	1849 Grayish cream wove paper; cotton rag; machine made; and with ruled lines	Light brown ink ICN rating: 1 CCI Fe ²⁺ : 10; Fe ³⁺ :50++
3	1864 Blue laid paper; cotton rag; hand made; chain and laid lines; and w/ ruled lines	Light brown ink ICN rating: 1 CCI Fe ²⁺ : ~25; Fe ³⁺ : ~25
4	1865 Blue ledger; laid cotton rag paper; hand made and with chain and laid lines	Light brown ink ICN rating: 1 CCI Fe ²⁺ : ~25; Fe ³⁺ : ~25
5	1841 Cream wove paper; cotton rag; machine made; and with ruled lines	Light brown ink ICN rating: 1 CCI Fe ²⁺ : ~25; Fe ³⁺ : ~25
6	1846 Cream wove paper; cotton rag; machine made; and with no ruling lines	Medium brown ink ICN rating: 1 CCI Fe ²⁺ : 50; Fe ³⁺ :50++
7	1846 Cream wove paper; cotton rag; machine made; and with no lines	Medium brown ink ICN rating: 1 CCI Fe ²⁺ : ~25; Fe ³⁺ : ~25
8	1875 Cream wove paper; cotton rag; machine made; and with thin blue lines	Light brown ink ICN rating: 1 CCI Fe ²⁺ : ~25; Fe ³⁺ : ~25
9	1846 Green wove paper; cotton rag; machine made and with no lines	Light brown ink ICN rating: 1 CCI Fe ²⁺ : ~10; Fe ³⁺ :~10

Table 1. Description of treated sample sets

resized with gelatin after washing as recommended by Gessa Kolbe for treated ink-corroded archival materials (2004).

Testing methods

Samples were tested extensively before treatment for media solubility in distilled water and in mixtures of ethanol and water (3:1, 1:1, and 1:3). Preliminary testing was carried out under magnification at 10X and 16X using a Zeiss microscope, Stemi SVII and with a thin sable brush (#000) dipped in the reagent, applied to heavily inked areas for thirty seconds and the surface observed for bleeding with a blotter. The water absorption of the nine samples was estimated by measuring the time the substrates absorbed a distilled water drop and then identifying the presence of sizing agents. Bathophenanthroline iron (II) ions test was performed on each document tested to assess the presence or recurrence of Fe²⁺ or Fe³⁺ ions before and after aqueous treatments (fig. 1). The non-bleeding indicator papers were examined and compared using the calibrated color chart developed at the CCI (table 1: media) and described the colors as 1: detectable; 10: weakly positive; 25: positive; and 50+:

	Treatment Sequences & Duration
1	Untreated control
2	Pure reverse osmosis (RO) water: pH 6.4; 20 min
3	Alkaline wash: pH 8.5 Ca(OH) ₂ ; 20 min
4	RO + 0.011M Ca(HCO ₃) ₂ : pH 6; 20 min each
5	RO + 0.086M Mg(HCO ₃) ₂ : pH 7.3; 20 min each
6	RO + Alkaline wash: pH 8.5 Ca(OH) ₂ ; 20 min each
7	Alkaline water simmer: pH 8.3 Ca(OH) ₂ ; 40°C; 15min
8	Alkaline water simmer: pH 8.3 Ca(OH) ₂ ; 90°C; 15min
9	Ethanol (EtOH) immersion, 15 min + alkaline water simmer: pH 8.3 Ca(OH) ₂ ; 40°C; 15 min each + sprayed EtOH
10	EtOH immersion, 15 min + alkaline water simmer: pH 8.3 Ca(OH) ₂ ; 90°C; 15 min each + sprayed EtOH
11	100% EtOH immersion; 20 min (used 95% Ethyl alcohol, denatured)
12	3:1 EtOH:RO; 20 min
13	1:1 EtOH:RO; 20 min
14	1:3 EtOH:RO; 20 min
15	Pre-wet with EtOH spray; calcium phytate: pH 5 (Ca-phy) + 0.011M Ca(HCO ₃) ₂ : pH 6; 20 min each
16	Ca-phy: pH5 + 0.011M Ca(HCO ₃) ₂ : pH6; 20min each
17	Ca-phy: pH 5 diluted 1:1:1 with RO: pH 5.5 and EtOH + 0.011M Ca(HCO ₃) ₂ : pH 6; 20 min each
18	Pre-wet with EtOH spray; Ca-phy (20 min) + water rinse: pH 5.5 (3x 10 min) + Ca(HCO ₃) ₂ (20 min)
19	Ca-phy:pH 5 (20 min) + water rinse: pH5.5 (3x 10 min) + 0.011M Ca(HCO ₃) ₂ (20 min)

Table 2.1. Aqueous treatments used

strongly positive. In the presence of Fe²⁺, the test strips turned a deep magenta, as there were observed upon application to untreated and treated inked areas. The study was carried out in May through July of 2002.

Surface pH measurements of the overall population (162 samples) were performed with a Beckman 60 pH Meter equipped with Beckman refillable combination (flat bulb, epoxy, AgCl, 12 x 155 mm electrode) in December 2004 (figs. 2–3,5). pH Measurements with cold water extraction were determined by using a glass microelectrode (Microelectrode Inc.) and recorded in June 2006 (figs. 4, 6).

Non-destructive instrumental analyses were carried out by Dr. Joseph Weber and the author at the Winterthur Museum

Table 2. Different Washing Treatments Used

No.	Treatments	Pre-wetting by spraying	Immersion 1	Immersion 2	Immersion 3	Pre-drying on suction table
1.	No treatment (control sample)	-	-	-	-	-
2.	Pure RO water pH6.4	-	RO (20 min, 20°C)	-	-	-
3.	Alkaline water pH8.5	-	RO+Ca(OH) ₂ (20 min, 20°C)	-	-	-
4.	RO + Ca bicarbonate pH6	-	RO (20 min, 20°C)	.01M Ca(HCO ₃) ₂ (20 min, 20°C)	-	-
5.	RO + Mg bicarbonate pH7.3	-	RO (20 min, 20°C)	.064M Mg(HCO ₃) ₂ (20 min, 20°C)	-	-
6.	RO + alkaline water pH8.5	-	RO (20 min, 20°C)	RO+Ca(OH) ₂ (20 min, 20°C)	-	-
7.	Hot alkaline water pH8.3	-	RO+Ca(OH) ₂ (15 min, 40°C)	-	-	-
8.	Hot alkaline water pH8.3	-	RO+Ca(OH) ₂ (15 min, 90°C)	-	-	-
9.	Alcohol + Hot alk. w. pH8.3	-	100% EtOH (15 min, 20°C)	RO+Ca(OH) ₂ (15 min, 40°C)	-	100% EtOH
10.	Alcohol + Hot alk. w. pH8.3	-	100% EtOH (15 min, 20°C)	RO+Ca(OH) ₂ (15 min, 90°C)	-	100% EtOH
11.	Alcohol	-	100% EtOH (20 min, 20°C)	-	-	-
12.	Alcohol/water mixture	-	3:1 EtOH/RO (20 min, 20°C)	-	-	-
13.	Alcohol/water mixture	-	1:1 EtOH/RO (20 min, 20°C)	-	-	-
14.	Alcohol/water mixture	-	1:3 EtOH/RO (20 min, 20°C)	-	-	-
15.	Phytate + deacidification	100% EtOH	Ca Phytate pH5 (20 min, 20°C)	.01M Ca(HCO ₃) ₂ pH6 (20 min, 20°C)	-	-
16.	Phytate + deacidification	-	Ca Phy pH5 (20 min, 20°C)	.01M Ca(HCO ₃) ₂ pH6 (20 min, 20°C)	-	-
17.	Phytate + deacidification	-	1:1:1 Ca Ph/RO/EtOH (20 min, 20°C)	.01M Ca(HCO ₃) ₂ pH6 (20 min, 20°C)	-	-
18.	Phytate + deacidification	100% EtOH	Ca Phy pH5 (20 min, 20°C)	RO pH5.5 X3 (10 min each rinse, 20°C)	.01M Ca(HCO ₃) ₂ pH6 (20 min, 20°C)	-
19.	Phytate + deacidification	-	Ca Phy pH5 (20 min, 20°C)	RO pH5.5 X3 (10 min each rinse, 20°C)	.01M Ca(HCO ₃) ₂ pH6 (20 min, 20°C)	-

Table 2.2. Individual sequences of wash combinations used in the study

Treatments	Sample Set 1	Sample Set 2	Sample Set 3	Sample Set 4	Sample Set 5	Sample Set 6	Sample Set 7	Sample Set 8	Sample Set 9
1. Control Fe (II) ions									
Control Fe (III) ions									
2. RO water									
3. Alkaline water									
4. RO+Ca (HCO ₃) ₂									
5. RO+Mg (HCO ₃) ₂									
6. RO+Alkaline w.									
7. Alkaline w. 40°C									
8. Alkaline w. 90°C									
9. EtOH+Alk.w. 40°C	N/A							N/A	
10. EtOH+Alk.w. 90°C	N/A							N/A	
11. 100% EtOH									
12. 3:1 EtOH/RO w.									
13. 1:1 EtOH/RO w.									
14. 1:3 EtOH/RO w.									
15. EtOH + Ca Phy + Ca (HCO ₃) ₂									
16. Ca P.+Ca (HCO ₃) ₂									
17. 1:1:1 Ca P./RO/EtOH + Ca (HCO ₃) ₂									
18. EtOH+Ca P.+RO3X + Ca (HCO ₃) ₂									
19. Ca Phy + RO 3X + Ca (HCO ₃) ₂	N/A		N/A		N/A	N/A		N/A	

Fig. 1. Bathophenanthroline Test: Corrosive Ferrous (Fe²⁺) and Ferric (Fe³⁺) Ions

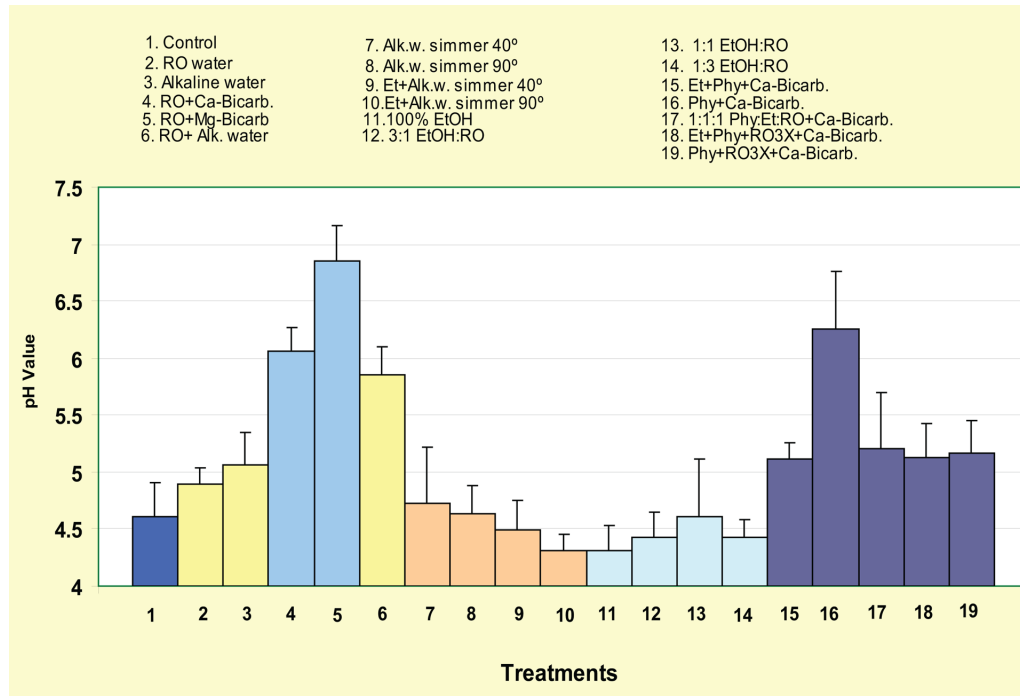


Fig. 2. Error bars represent the population standard deviation from the pH averages of each of the 18 aqueous treatments used and the untreated control samples recorded with surface pH measurements.
Part 1 - pH of 9 Iron Gall Ink Paper Samples Standard Deviations (recorded with a surface electrode)

to identify the inorganic components of inks and papers used in this study. Energy dispersive x-ray fluorescence spectroscopy (ED-XRF) with an ArtTAX iXRF spectrometer. X-ray fluorescence consistently established the presence of iron as the only major element. The presence of gelatin size in the samples was determined by Season Tse at the Canadian Conservation Institute using Fourier transform infrared spectroscopy-attenuated total reflection (FTIR-ATR) with a Travel IR ATR-IR spectrometer (SensIR Technologies, Smiths Detection) (table 3).

Evaluation of Side Effects

Visual assessment was conducted of the entire population of samples under magnification, daylight, and UV-fluorescence to identify color changes, dissolution of ink compounds, crystal formations, and immediate side effects after washing. Visual side effects of media and substrates were recorded in daylight and UV-fluorescence photography using a digital camera, (Olympus E-10, 4,0 megapixel).

SUMMARY OF RESULTS

Aqueous Washing at Room Temperature

Most papers washed with aqueous treatments at 20° C looked lighter than the untreated control samples. All aqueous treatments removed the thin, blue, ruling lines present

Samples	Substrates	Media
1. 6.28.1856	FTIR-ATR: gelatin μXRF-paper: Fe, Ca, K, Cl, S	μXRF-ink: Fe, K
2. 12.13.1849	FTIR-ATR: no gelatin μXRF-paper: Fe, Zn, Cu, Ca, Mn, K	μXRF-ink: Fe, K, Ca
3. 7.6.1864	FTIR-ATR: gelatin μXRF-paper: Ca, S, Fe, K, Cu	μXRF-ink: Fe, Ca, S
4. 12.31.1865	FTIR-ATR: gelatin μXRF-paper: Ca, Fe, Mn, Cu, Zn, S, Cl	μXRF-ink: Fe, Zn, Cu, K, S
5. 6.8.1841	FTIR-ATR: no gelatin μXRF-paper: Fe, Ca, K, Mn, Cl	μXRF-ink: Fe, K, Cu, Ca, Zn
6. 10.5.1846	FTIR-ATR: gelatin μXRF-paper: K, Ca, Cu, Fe, Co, S	μXRF-ink: Fe, K, Ca
7. 10.6.1846	FTIR-ATR: gelatin μXRF-paper: K, Co, Cu, Fe, Ca, Ni, S	μXRF-ink: Fe, Co, K, Cu, Zn
8. 3.22.1875	FTIR-ATR: no gelatin μXRF-paper: Fe, Ca, K, Cl, Ti	μXRF-ink: Fe, K, Ca
9. 4.5.1846	FTIR-ATR: no gelatin μXRF-paper: Fe, Ca, K, Cl, Ti, S	μXRF-ink: Fe, Cu, Mn, Ca, Cl, K

Table 3. Instrumental Analyses: FTIR and XRF

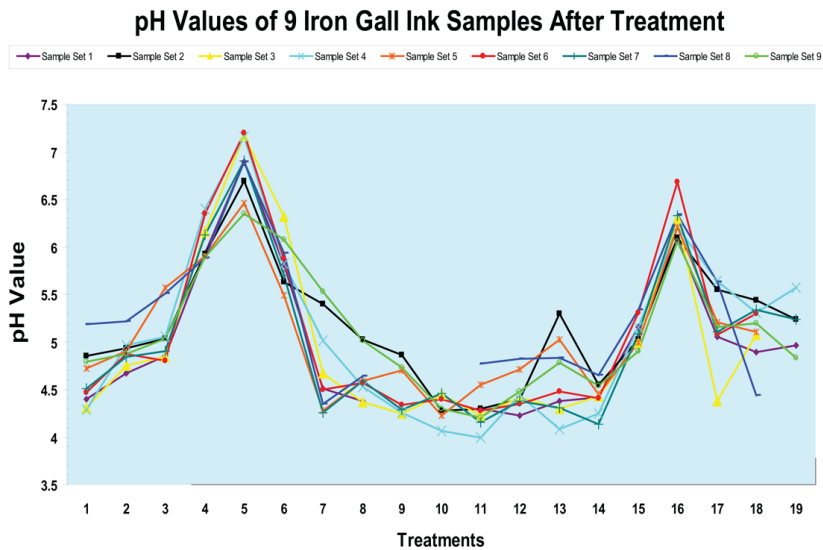


Fig. 3. pH Measurements—Surface Electrode Recorded in Dec. 2004

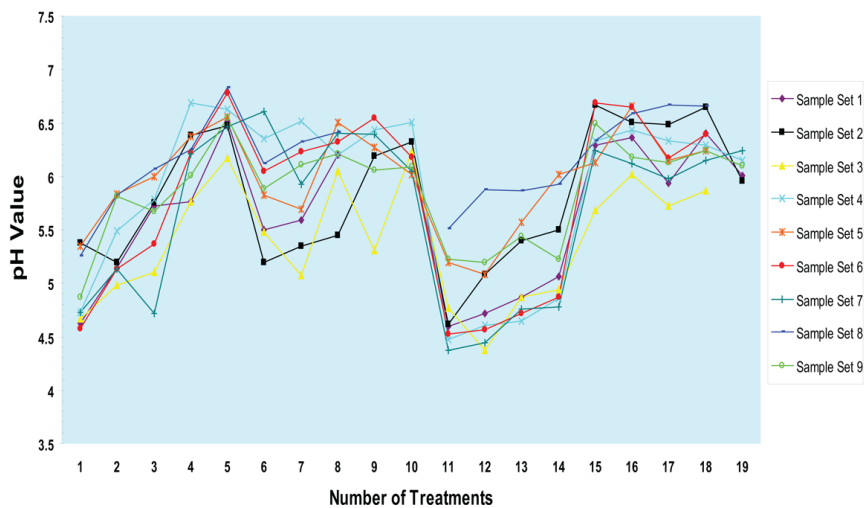


Fig. 4. pH Measurements—Cold Water Extraction Recorded in June 2006

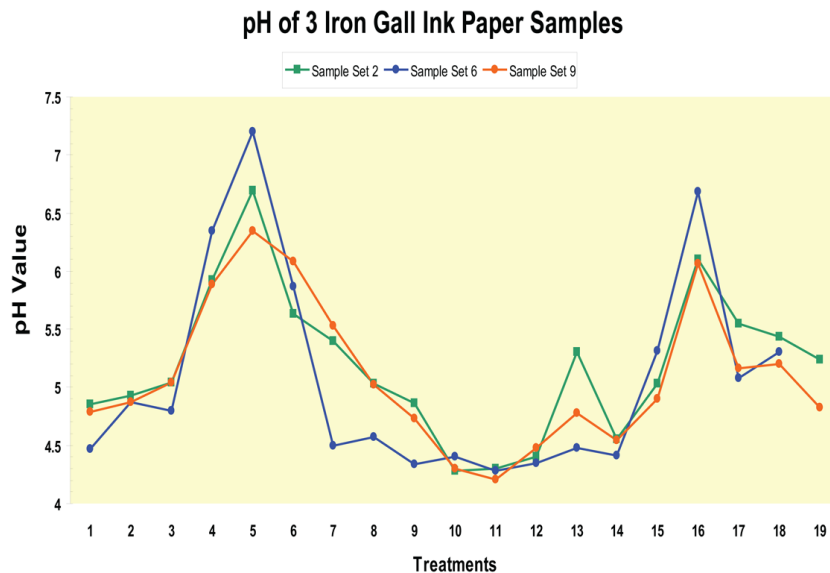


Fig. 5. pH Measurements—Surface Electrode Recorded in Dec. 2004

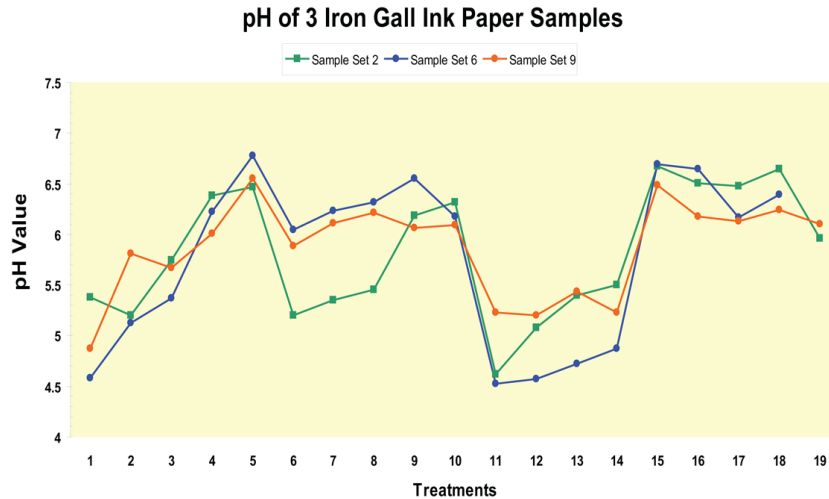


Fig. 6. pH Measurements—Cold Water Extraction Recorded in June 2006

on most samples. The more water that was used in the treatments, the more these lines were removed. From all the aqueous treatments at 20° C used (#2, #3, and #6), the one that removed most Fe²⁺ and resulted in the least bleeding of inks was RO+alkaline water (#6). The pH values of aqueous treatments at 20° C were higher than the results obtained with all aqueous washing at increased temperature treatments, with and without alcohol (#7, #8, #9, and #10) and baths of 100% alcohol and mixtures of water+EtOH solutions, e.g., 3:1; 1:1; and 1:3 (#11, #12, #13, and #14).

Aqueous Deacidification

In many samples deacidified with calcium or magnesium bicarbonates solutions (#4 and #5) the papers looked slightly darker than RO+alkaline water (#6). Some samples showed a slight bleeding of the inks with both calcium and magnesium bicarbonate deacidification solutions. Both calcium and magnesium bicarbonate removed most of Fe²⁺ and few samples showed slight deposits across the papers after treatments. The traces of Fe²⁺ were quite similar, but samples treated with calcium bicarbonate appeared to have better results overall than those treated with magnesium bicarbonate. All the samples treated with magnesium bicarbonate achieved the highest pH values after treatments.

Aqueous Washing at Increased Temperature

By elevating the water temperature to 90° C (#8 and #10), the efficiency of washing the papers increased. Daniels and Kosek have had similar results (2002); more soluble Fe²⁺ ions and water-soluble components seemed to be removed. Overall, the papers appeared much cleaner and lighter in color. The increase in flexibility and brightness in the substrates is likely caused by the removal of sizing and fillers. Generally, all the samples subjected to simmering water treatments (#8 and #10) looked the brightest, inks became duller,

and the colors of both inked lines and papers were affected. When examined under UV-fluorescence illumination (figs. 3–4), all the samples treated with simmering water washing have a very distinctive appearance; this is probably due to the removal of sizing (gelatin), calcium sulfate (gypsum) filler, and other additives. The pH values (measured with a surface electrode) after simmering were quite low, ranging from pH 4.04 to pH 5.53. Cold water extraction results trended toward an increase in pH with simmering (Tse 2008) (figs. 3–6). The samples treated in this study with simmering water washing were not deacidified.

Alcohol and Water: Alcohol Mixtures

Because the dissolution of the ink compounds was different in the nine sample sets, the various combinations of alcohol and mixtures of water and alcohol were studied to assess the ability to protect the media. Ethanol seemed to prevent damage, such as bleeding, ink blurring, and color change. Alcohol is known to lower the surface tension of water, promoting fast and even penetration and improving wettability of both the inked lines and paper supports. The use of alcohol limits the migration of the inks and the brown haloing effect that is apparent when using only aqueous treatments. It appears from this study that the more EtOH used in the solutions, the less effective the removal of Fe²⁺ discoloration of paper, and other water-soluble materials. The addition of EtOH to various aqueous treatments decreased the water content of the solutions and limited the solubility of water-soluble degradation products. From all the combinations tested, the 1:1 EtOH:RO solution (#13) produced the least bleeding in comparison with other aqueous treatments (#2, #3, and #6) but had an undesired effect of reducing the extraction of Fe²⁺ ions after treatment. Possibly, this could cause a risk of continued degradation of the paper in the future.

Ca-Phytate + Ca-Bicarbonate Solution

From the five calcium phytate treatments used, the best visual results and the least side effects were achieved with calcium phytate/calcium bicarbonate (#16). This treatment seems also to be the most effective in delaying ink corrosion as well as depositing an alkaline reserve in the papers. This was evident from the Fe²⁺ tests and pH values obtained from all the samples treated with the chelating agent followed by deacidification. Most of the Fe²⁺ ions were removed during aqueous phytate treatments and overall there were no traces across the papers after washing. Additionally, no white calcium phytate precipitates were found on the surface of the papers and inks following the treatments. These deposits can be caused by the low solubility of calcium phytate and favorable results were obtained with pH 5. The pH values were overall slightly higher than the results obtained with deacidification with calcium bicarbonate (#4). When using calcium phytate plus calcium bicarbonate (Ca-Ph+Ca bicarb.), no visual changes in the ink colors and in paper appearances were observed. After bathing, the discoloration present in the papers seemed to be reduced much more than with the treatment option employing the addition of ethanol as a wetting agent (#15).

CONCLUSIONS

The combined treatment using calcium phytate and calcium bicarbonate proved to be the most effective, causing the least side effects and thus providing the most lasting protection (Tse et al. 2006; Tse et al. 2009). Phytate does not destroy iron (III) gallotannates and deactivates iron, but no other transition metals such as Cu, Zn, Mn, Al, Mg, CO, and Ni (Neevel 2008).

Visual examination showed that there were not many differences in yellowing of papers and browning of inks when calcium or magnesium bicarbonate solutions were used. Research has shown that a single deacidification treatment with calcium or magnesium bicarbonate solutions is not sufficient to prevent ink corrosion because the Fe (II)-catalyzed oxidation is only blocked temporarily, since Fe (II) ions are oxidized in an alkaline environment to Fe (III) ions (Reissland 1999). A combined treatment with aqueous calcium phytate and calcium bicarbonate provides a better protection than aqueous calcium bicarbonate alone (Neevel 2008).

The aqueous washing treatments with increased temperatures at 40° C and 90° C caused substantial color changes in both the inks and papers, and especially the treatments that were pre-dried with a suction table (#9 and #10) that removed the sizes and dyes or pigments from colored papers. Visually the results obtained with simmering water washing were the least desirable treatment options.

The results from this study concluded that the more alcohol in the solution, the less effective the removal of Fe (II)

ions and other water-soluble degradation components. Both Reissland (1999) and Eusman (2006) have had similar results. Conservators should consider to what extent it is necessary to preserve the original characteristics of the papers and inks, such as dyes or pigments in colored papers, ruling lines, and variation in the colors of the inks caused by the presence of additives or impurities, e.g., natural dyes, logwood, indigo, Brazilwood, and aniline dyes.

All aqueous treatments removed most of the iron (II) ions, and there were no deposits across the papers tested with indicator paper to identify iron (II) ions present as salts in the paper. The more water that was involved with the treatments, the more discoloration was removed from the papers, but occasionally the inks bled or appeared slightly dull after treatments. The test for iron (II) ions, Bathophenanthroline, has proven to be a useful tool for conservators to monitor the presence of free iron ions on the media and paper and within the washing solutions.

Resizing with gelatin should be considered after simmering water treatments and most stabilization treatments of ink-corroded archival materials (Kolbe 2004).

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MATERIALS

Bathophenanthroline iron (II) ion test

PEL - Preservation Equipment Ltd.

Norfolk, UK

www.preservationequipment.com

NOTES

1. For more on currently used and newly developed aqueous treatments see Biggs 1997; Biggs et al. 2006; Choi and Zinsmeister 2006; Connelly et al. 2006; Eusman and Mensch 2001; Fleischer et al. 2006; Heller et al. 1993; Hofmann 2007; Kolar and Strlič 2001; Kolar and Strlič 2004; Kolar et al. 2003; Kolar et al. 2005; Kolar and Strlič 2005; Kolar et al. 2007; Neevel 1995; Neevel 1995a; Neevel 2001; Neevel and Reissland 1997; Neevel and Reissland 2001; Orlandini 2006; Orlandini et al. 2008; Reissland 1999; Reissland 2000; Reissland and de Groot 1999; Reissland and Hofenk de Graaff 2000; Reissland et al. 2007; Sistach 2007; Trojan-Bedynski et al. 2003; Tse et al. 2005; and Tse et al. 2009.

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