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A Comparison of Aqueous Versus Ethanol Modified Calcium Phytate Solutions for the Treatment of Iron Gall Ink Inscribed Paper

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While the calcium phytate/calcium bicarbonate treatment has proven to be effective in delaying iron gall ink corrosion on paper, this aqueous treatment cannot be used safely on documents with water soluble iron gall inks. This study explores the efficacy of ethanol diluted calcium phytate. Laboratory prepared iron gall ink with excess iron ions was applied to a nineteenth century ledger paper to create samples that were then treated with six variations of calcium phytate solution with and without ethanol modification, and with and without alkaline washing. They were subjected to accelerated heat aging at 90°C for 14 days. The unaged control and aged samples were tested with bathophenanthroline iron (II) test papers, zero-span tensile strength, pH and colour measurements, and inductively coupled plasma atomic emission spectrometry (ICP-AES) multi-element scan. Results after heat aging showed that all variations of phytate solution, without further deacidification, were able to reduce the loss of strength in paper with and without ink. Treatment with undiluted phytate (100%) with or without alkaline washing offered the best protection. Inks without alkaline washing retained more iron ions in the ink and as a result retained more phytate. Dilution of the aqueous phytate solutions with ethanol reduced its ability to remove acids, hence reducing its ability to protect paper from strength loss. Repeated applications of the ethanol modified solutions resulted in the accumulation of more phytate on the paper and ink, and delayed the recurrence of iron (II) ions.

Bien que les résultats de travaux de recherche démontrent que le traitement au phytate de calcium et au bicarbonate de calcium retarde efficacement la corrosion causée par l'encre ferro gallique présente sur des œuvres de papier, cette méthode basée sur l'emploi d'une solution aqueuse ne peut être utilisée pour traiter sans danger des documents contenant des encres ferro galliques hydrosolubles. La présente étude avait pour but de déterminer l'efficacité du phytate de calcium dilué dans l'éthanol comme solution de traitement. Une encre ferro gallique contenant un excès d'ions fer préparée en laboratoire a été appliquée sur un papier registre datant du XIXe siècle afin de produire des échantillons qui ont ensuite été traités avec six solutions différentes de phytate de calcium, modifié ou non à l'éthanol, et avec ou sans lavage alcalin. Les échantillons ont été soumis à un traitement de vieillissement thermique accéléré, à 90°C, pendant 14 jours. Les échantillons témoins non traités et les échantillons vieillis ont été mis à l'épreuve à l'aide de papiers d'essai permettant de déterminer la présence d'ions Fe(II) au moyen de la bathophénanthroline, ainsi qu'en réalisant des essais de résistance à la rupture par traction, des mesures du pH et de la couleur, et des analyses multiéléments par spectroscopie d'émission atomique couplée à un plasma inductif (ICP AES). Les résultats obtenus pour les échantillons vieillis thermiquement indiquent que toutes les solutions de phytate de calcium permettent, et ce, sans désacidification ultérieure, de réduire la perte de résistance du papier, en présence ou non d'encre ferro gallique. Le traitement assurant la meilleure protection est celui réalisé avec du phytate de calcium non dilué (100 %), avec ou sans lavage alcalin. L'encre des échantillons n'ayant pas été traités par lavage alcalin a une teneur plus élevée en ions fer et, conséquemment, fixe de plus grandes quantités de phytate de calcium. La dilution des solutions aqueuses de phytate de calcium avec de l'éthanol réduit leur capacité d'éliminer les acides et, par conséquent, leur capacité de protéger le papier contre la perte de résistance. L'application répétée des solutions de phytate modifié à l'éthanol entraîne une accumulation de phytate supplémentaire à la surface du papier et de l'encre et retarde la réapparition des ions Fe(II).

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Introduction

Chemistry of Iron Gall Ink

The chemistry of iron gall inks and their corrosive effects on paper and parchment have been a subject of scientific study for more than 350 years.[1] Much of our present understanding of the causes and mechanisms of paper deterioration by iron gall inks is a result of concentrated efforts made by researchers in the Netherlands;[2-9] by three major European collaborative projects: InkCor,[10] Papylum[11,12] and Transition Metals in Paper;[13] by the Austrian National Library and the State Academy of Art and Design Stuttgart in Germany;[14,15] by the US Library of Congress;[16-18] and by the University of Natural Resources and Life Sciences in Vienna (BOKU).[19-24]

Beginning with a clear description of the ink chemistry and the structure of the ink complex provided by Krekel,[25] the corrosive effects of iron gall inks on paper are attributed to its acidity, which leads to acid catalyzed hydrolysis of cellulose, and to the presence of excess iron (II) ions in some inks, which catalyze the oxidation of cellulose via the Fenton reaction.[2] Common symptoms of this corrosion are darkening of the paper near the ink area and brittleness and loss in the ink area. Not all iron gall inks are equally corrosive. The degree of damage appears to be a function of the ink composition and quantity, the properties of the paper,[4,26] and the environment, specifically elevated temperature and humidity.

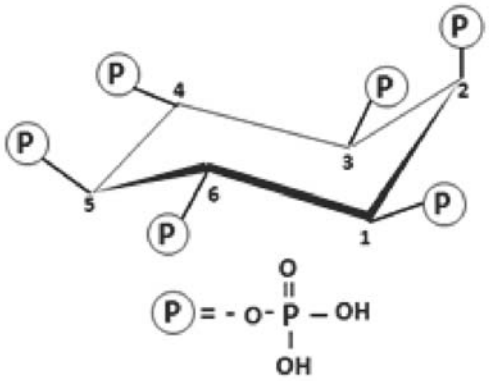

Figure 1. Structure of phytic acid in dilute solutions.[41]

Calcium Phytate / Calcium Bicarbonate Treatment

A number of analytical techniques, diagnostic tools and effective remedial measures for corrosive inks have been developed.[3,10,14,26,27-30] Among these is the combination phytate-bicarbonate treatment. Since its introduction in 1995,[2] the phytate-bicarbonate treatment for iron gall ink documents remains one of the most tried and proven treatments for inhibiting ink corrosion of paper.[8,14,31-36] The treatment has also been used on black-dyed cellulosic,[37] silk textiles,[38] black-dyed spruceroot baskets[39] and for the stabilization of rust stained prints.[40]

Phytic acid, hexaphosphorylated *myo*-inositol (**Figure 1**), is a major component of plant seeds, protecting seeds from oxidative damage during storage.[42] As an antioxidant, it has a very high affinity for iron, forming a unique iron chelate with all six coordination sites occupied, thus inhibiting iron-catalyzed oxidative reactions. Both calcium[8,14,31-36] and magnesium phytate[34] have been shown to be effective antioxidants.

In the treatment of iron gall inks, phytate has an additional benefit. Unlike chelators such as EDTA or DTPA, the phytate-iron complex is not so strong that it destroys the ink complex.[6,7] In addition, the low water solubility of the iron-phytate complex means that phytate is able to prevent lateral migration and loss or removal of iron (II) ions during aqueous treatments.[15] The subsequent bicarbonate treatment neutralizes the remaining acids in the ink, and forms a buffer which provides protection from future acidification. This combination chelation/deacidification treatment offers unparalleled protection for iron gall ink inscribed documents and objects containing iron.

A detailed description of the optimized protocol for this treatment can be found at the Ink Corrosion Website.[9] A summary of phytate research, and standard treatment considerations and protocols were published by Huhsmann and Hähner.[43] The treatment is also included in the guidelines for iron gall ink treatment published by the Library of Congress.[18]

Ethanol Modified Calcium Phytate / Calcium Bicarbonate Treatment

Despite these benefits, as an aqueous treatment the phytate treatment has limitations. Documents inscribed with water soluble iron gall inks cannot be immersed in an aqueous calcium phytate solution. To overcome this, one option is to modify the phytate solution by adding ethanol – a solvent commonly used for pre-wetting paper prior to washing. Calcium phytate is not soluble in 100% ethanol, but can remain in solution in a mixture of as little as 25% aqueous solution of calcium phytate and 75% ethanol. These solutions can sometimes be safely used for the treatment of inks in documents with water soluble inks.

Dilution with ethanol reduces the concentration of phytate in a solution and is therefore expected to reduce the degree of protection for paper inscribed with iron gall inks. Evidence of this was reported by Duplat et al.[40] and found during previous research by the Canadian Conservation Institute (CCI) and Library and Archives Canada, where the use of ethanol and water diluted calcium phytate (33%) resulted in some recurrence of Fe(II) ions after heat aging of the samples.[35,36] The Library of Congress treatment guidelines for iron gall ink inscribed materials include ethanol modified phytate as a treatment option,[18] but because the solution is expected to be less effective the guidelines recommend diluting the solution no more than 50% with ethanol.

Even with the existing recommendations, conservators considering this treatment option still have the following questions:

- Does dilution with ethanol reduce the effectiveness of calcium phytate? By how much?
- Does the efficacy of calcium phytate diminish significantly at a certain percent dilution?
- Do repeated applications of ethanol diluted phytate increase its efficacy?

This study aims to address these questions by verifying the benefits of ethanol diluted calcium phytate at different concentrations, and by evaluating the efficacy of repeated applications of fresh ethanol modified phytate. In order to isolate the effect of phytate, which could be masked by deacidification, the calcium bicarbonate deacidification step was deliberately not performed on the samples.

The second goal of this study is to further investigate the effect of eliminating alkaline water washing in the treatment of iron gall ink documents. Alkaline washing is a common treatment step employed prior to other aqueous treatments of works on paper but its use is obviously problematic for documents that contain water soluble inks. However, researchers have noted the possible benefits of eliminating this step from a calcium phytate/calcium bicarbonate treatment.[33,44]

Sample Preparation and Treatment Procedures

Preparation and Application of the Ink

The ink with excess iron (II) (Fe:tannic acid ratio of 5.5:1) was prepared according to the method described by Neevel.[2] Gum arabic (acacia; 15.70 g) was dissolved in water purified by reverse osmosis followed by deionization (500 mL). This

mixture was heated on a hot plate until all the gum was dissolved. After cooling to room temperature, ferrous sulphate (21g; $FeSO_4.7H_2O$; Mwt 278.01 g/mol) and tannic acid (24.6 g; 90%; 1701.28 g/mol) were slowly added to the gum mixture with stirring. The insoluble precipitate in the ink was allowed to settle prior to its application on the paper in order to ensure an even deposition of ink. The ink had a blue-black appearance and a pH of 2.0.

The paper chosen to make the samples was a blue rag ledger paper c.1850 with "Superfine Record linen paper" watermark and starch and alum size. Paper like this is often found inscribed with iron gall inks in Canadian collections. This paper was also chosen because its lower absorbency would permit better observation of the effectiveness of phytate in inhibiting lateral migration and migration of ink through the paper. The ink (50 µL) was applied to the paper with a precision control lab pipette and spread evenly with a plastic spatula. The ink did not penetrate to the verso. The resulting ink lines measured 1 cm x 22 cm. A spatula rather than a brush was used to spread the ink in order to better ensure that all the ink lines were composed of the same volume of ink per area. Had a brush been used some of the measured quantity of ink would have been absorbed into the brush bristles. Any unevenness in ink application was compensated for by averaging the results from nine ink lines per treatment group. After air drying, the ink on the samples was set by oven drying at 70°C for 72 hours.

Preparation of the Calcium Phytate and Ethanol Mixtures

Calcium phytate solution was prepared following the procedure of Reissland and Ligterink.[9] Phytic acid solution (2.88 g; 40%) was weighed into a 100 mL beaker. Calcium carbonate (0.44 g) was added to the phytic acid in small portions, and stirred to avoid the formation of lumps. Deionized water (100 mL) was added to dissolve the mixture. The resulting calcium phytate solution was transferred to a 1 L beaker and diluted to 1 L. The pH of this solution was measured using an Orion 210A pH meter with an Orion combination pH electrode. The pH of the calcium phytate solution was adjusted from pH 2.9 to 5.8 using an ammonium hydroxide solution (1.4%; 9.5 mL). The calcium phytate concentration in the final solution was 1.75 mmol/L.

Alkaline water, used for washing, was prepared by adding saturated calcium hydroxide solution to reverse osmosis/deionized water until the pH was 8.5. The 50:50 ethanol-calcium phytate solution was prepared by adding 500 mL of anhydrous ethanol to 500 mL of calcium phytate solution. The 25:75 solution was prepared by adding 750 mL of ethanol to 250 mL of calcium phytate solution.

Experimental Treatment and Aging of the Samples

The samples were cut into 11 cm x 11 cm sheets, each having three ink lines and weighing 1.5 g. Three replicates were prepared for each treatment solution, with a ratio of 1.5 g of sample to 300 mL of solution. A description of each experimental treatment solution and procedure used can be found in **Table I**. The ink samples were supported on Reemay, sprayed with 100% ethanol and then immersed in separate baths of the solutions. For repeated immersion samples, P25(2X) and P25(3X), fresh solutions of calcium phytate were used for each application. After immersion, the samples were placed on a paper suction table[9] in order to quickly remove any excess liquid that might cause lateral migration of the ink, then removed and dried between blotters under light weight.

The total immersion time for each experimental treatment was kept constant at 30 minutes. While the duration of actual treatments can vary according to the requirements of an object, the most commonly used immersion time for a calcium phytate treatment is 20 minutes.[18,35,43] In this study a total immersion time of 30 minutes was used – a maximum recommended immersion time for a phytate treatment[9] – in order to maximize the complexation of the phytate with the Fe(II) ions in the ink.

Heat aging was carried out in sealed tubes according to the ASTM standard test method D 6819-02.[45] Details of the method have been described by Bégin and Kaminska.[46] Prior to accelerated heat aging, the controls and treated samples were preconditioned at 30°C for 2 hours in a dry oven, and then conditioned for 2 days in an environmentally controlled room (50 ± 2% RH; 22 ± 0.2°C) before putting them in tubes (144 mL Lab-Line No.308-9 hybridization tubes with polypropylene screw cap and a Teflon gasket). The humidity inside the tubes was not measured; it is dictated by the moisture content of the paper samples and is kept constant by using hermetically sealed tubes. Each tube contained 4.2 g of sample from the same treatment, and was placed in a precision control oven (Fisher Isotemp 718F) at 90°C for 14 days. **Figure 2** shows the ink samples and the tube used for aging.

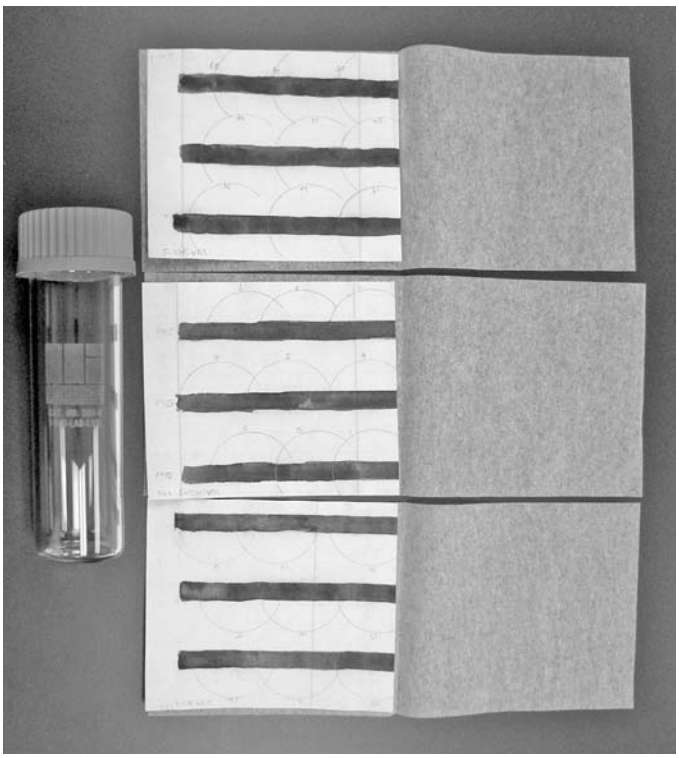

Figure 2. A set of samples for one treatment group and a Lab-line hybridization tube used for heat aging.

Table I. Description of Experimental Solutions and Procedures.

Code	Experimental Solutions	Procedure
C1	Untreated	Untreated control
C2	Alkaline wash	Alkaline water wash: 30 min in pH 8.5 calcium hydroxide water; 5 min suction table; dried between blotters under light weight
C2+P100	Alkaline wash + 100% Phytate	Alkaline water wash: 15 min in pH 8.5 calcium hydroxide water; 15 min in calcium phytate; 5 min suction table; dried between blotters under lightweight
P100	100% Phytate	30 min in calcium phytate; 5 min suction table, dried between blotters under light weight
P50	50:50 Phytate:ethanol	30 min in 50:50 phytate:ethanol; 5 min suction table, dried between blotters under light weight
P25	25:75 Phytate:ethanol	30 min in 25:75 phytate:ethanol; 5 min suction table, dried between blotters under light weight
P25(2X)	25:75 Phytate:ethanol (2X)	15 min in 25:75 phytate:ethanol; 5 min suction table, dried between blotters under light weight; repeated twice
P25(3X)	25:75 Phytate:ethanol (3X)	10 min in 25:75 phytate:ethanol; 5 min suction table, dried between blotters under light weight; repeated three times

Methods of Analysis

Colour measurements were used to monitor the change in the ink colour and the colour of the paper verso to the ink as a result of treatment and heat aging. Measurements were carried out using a Minolta Chromameter CR300. For each experimental treatment, a total of 27 measurements were carried out for each ink line and paper verso to the ink line, before and after treatment, and after heat aging. Change in lightness (L*), red-green (a*), yellow-blue (b*) and total colour change (delta E '76) for the ink and paper were calculated to determine the effects of the treatments and aging. After colour measurement, the samples were subjected to zero-span tensile strength tests.

Zero-span tensile strength measurements were done using a Pulmac Zero-span Tensile Strength tester with the pressure set at 552 kPa (80 psi), according to TAPPI standard T231,[47] in an environmentally controlled room (50 ± 2% RH; 22 ± 0.2°C). Testing was carried out on paper samples with and without ink in the machine-direction for untreated control samples and for all samples after aging. Multiple measurements were completed for each experimental treatment group and the results averaged. The paper fragments from this test were used for cold extraction pH and multi-element scan.

Cold extraction pH was carried out using an Orion Ionanalyzer EA940 with an Orion Ultra-flat ROSS ion selective electrode, following a modification of TAPPI standard T 509[48] to accommodate a sample size of less than 1 gram. Unaged control and aged paper samples with and without ink (0.14 g) were extracted with water purified by reverse osmosis and deionization (10 mL for 1 hour prior to pH measurement of the extract. Duplicate measurements of the samples were carried out. The pH of the purified water was 5.98 as measured using ionic strength adjustor.

Inductively coupled plasma atomic emission spectrometry (ICP-AES) multi-element scan was carried out by Caduceon Environmental Laboratories, Ottawa.[49] Triplicates (0.2 g paper with ink and 0.5 g of paper without ink each) of unaged untreated controls and of treated samples after aging were analyzed.

Bathophenanthroline iron (II) test strips were used to test the inks[27,28] before and after treatment, and after aging. The colour of the test papers was recorded using the colour chart developed at the CCI for the test strips.[35] The test papers were then mounted and photographed. Since the study's main concern was the chelation of Fe(II) ions by phytate, further testing for iron (III) ions using ascorbic acid or dithionite[50] was not carried out.

Results and Discussion

Bathophenanthroline Tests Results

The results of the iron (II) tests using bathophenanthroline test strips are summarized in **Table II**. The test strips were originally developed as a diagnostic tool for the presence of Fe(II) ions in iron gall inks. Before treatment, all the inks had a high concentration of free Fe(II) ions of 50+. This is expected as the ink contained excess iron in a ratio of 5.5:1, Fe:tannic acid. All the aqueous treatments and 50% ethanol modified treatment solutions (P50) were able to remove all the free Fe(II) ions through a combination of dissolution and complexation. The single immersion of 25% ethanol modified treatment solution (P25) was the least effective in removing the Fe(II) ions, but repeating the applications twice (P25(2X)) or three times (P25(3X)) improved the effectiveness.

Heat aging can cause the formation of additional Fe(II) ions in treated samples.[27,35] The concentration of free Fe(II) ions increased after heat aging for all treatment groups (**Table II**) but

Table II. Bathophenanthroline iron (II) tests results for concentrations of available Fe(II) ions in the ink before and after treatment, and after aging (0-<1: no; 1-10: low; 10-25: medium; 25-50+: high).

Code	Treatment Solutions	Before treatment			After treatment			After Aging		
		Test 1	Test 2	Test 3	Test 1	Test 2	Test 3	Test 1	Test 2	Test 3
C1	Untreated	25	50+					25-50	25-50	
C2	Alkaline wash	50+	50+	50+	0	0	0	25+	25+	25-50
C2+P100	Alkaline wash +100% Phytate	50+	50+	50+	0	0	0	1	1	1-10
P100	100% Phytate	50+	50+	50+	0	0	0	0-<1	0-<1	0-<1
P50	50:50 Phytate:ethanol	50+	50+	50+	0	0	0	0-<1	0-<1	0-<1
P25	25:75 Phytate:ethanol	50+	50+	50+	1-25	1-25	1-25	25+	25+	0-<1 (mottled)
P25(2X)	25:75 Phytate:ethanol (2X)	50+	50+	50+	10	10	1-10	10-25+	10-25+	25+
P25(3X)	25:75 Phytate:ethanol (3X)	50+	50+	50+	1	0-<1	0	10	10	10-25

to varying degrees. The ranking from least to most formation of Fe(II) ions is:

P100 ≈ P50 ≈ C2+P100 < P25(3X) ≲ P25(2X) ≲ P25 ≈ C2 < C1

The intensity of the Fe(II)-bathophenanthroline complex is a function of the concentration of available or free Fe(II) ions in the ink, and not the total concentration of iron ions in the test area. Since the presence of free Fe(II) ions is responsible for catalyzing cellulose oxidation, all other factors being equal, it is reasonable to believe that the higher the concentration of the free Fe(II) ions, the higher the risk of corrosion. The effectiveness of a treatment solution is indicated by the concentration of free Fe(II) ions detected after treatment and after heat aging. An effective treatment will not only remove free Fe(II) ions, it will also be able to delay the recurrence of these ions after accelerated aging. The bathophenanthroline results suggest that a 50% solution of ethanol modifed calcium phytate may be as effective as a 100% calcium phytate solution. The test strips show that alkaline washing (C2) alone is the least effective treatment as it results in the greatest recurrence of Fe(II) ions[27,28] even though it removes all free Fe(II) ions initially. Although repeated application of calcium phytate resulted in lower free Fe(II) iron concentrations initially, the 25% solutions of calcium phytate were less effective at reducing concentration after treatment and delaying recurrence after aging.

Colour Measurements

Ink after Treatment and Aging

All the treatments resulted in visible darkening of the ink (decrease in L*) (**Figure 3**). The inks became slightly more yellow/less blue (increase in b*) and more red/less green (increase in a*). This change in chroma (a* and b*) is greater among the aqueous phytate samples, C2+P100 and P100, and P50. The dominant contributor to the total colour change (dE'76) of the ink is the decrease in lightness (L*). The treatment that showed the least total colour change immediately after treatment is P50.

After heat aging, all the inks darkened further (decrease in L*) and became more yellow or less blue (increase in b*) (**Figure 4**). The untreated control (C1) darkened the most in comparison to the treated samples; the increase in a* and b* is similar to the treated inks. While the aqueous treated samples, C2, C2+P100 and P100, showed less darkening (L*), the change in chroma is similar to P25, P25(2X) and P25(3X). P50 showed slightly greater change in a* and b* compared to the other samples.

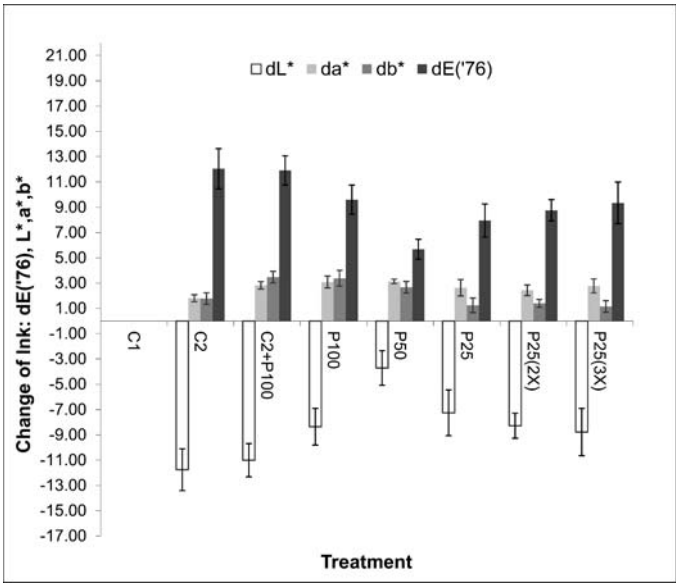

Figure 3. Colour change of ink (mean and standard deviation) after treatment.

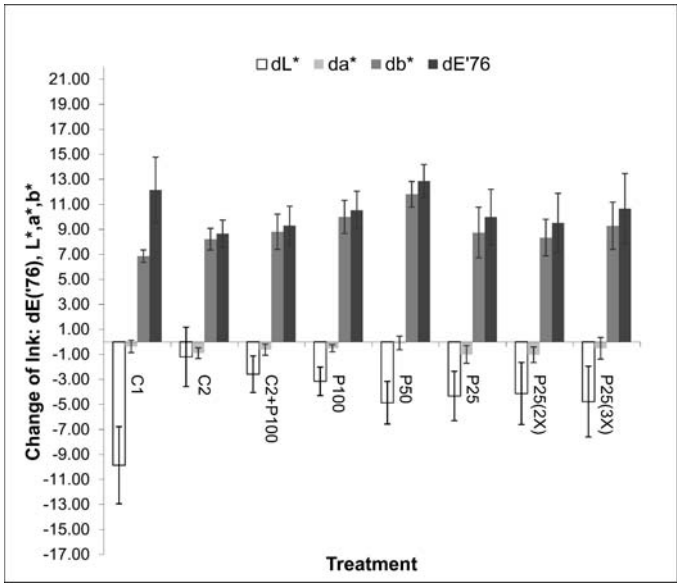

Figure 4. Colour change of ink (mean and standard deviation) after heat aging.

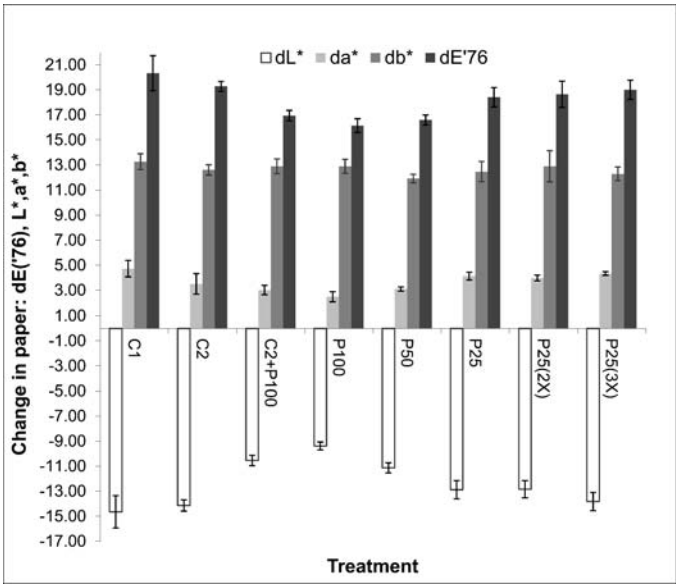

Figure 5. Colour change of paper verso to ink (mean and standard deviation) after heat aging.

Paper after Treatment and Aging

Because of the starch and alum size, the blue ledger paper was not very absorbent; therefore, there was no penetration of the ink through to the verso of the paper after application. After treatment there was very little measurable colour change in the paper: all the papers became slightly less yellow (decrease in b*).

All papers after heat aging became visibly more yellow (b*) to the same degree with or without treatment (**Figure 5**). The untreated control, alkaline washing alone (C2) and the three P25 samples all darkened (L*) to a similar degree, while the treatments that resulted in the least amount of darkening were:

P100 < C2+P100 ≲ P50.

Darkening of the ink area on the verso of the paper after heat aging is an indicator of corrosion.[4] The treatment solutions that resulted in the least darkening, P100, C2+P100 and P50, were the same ones that exhibited the least recurrence of free Fe(II) ions after heat aging in the bathophenanthroline tests.

ICP-AES Analyses of Paper with and without Ink

Atomic emission spectrometry provided quantitative results showing the elemental ions in paper with and without ink after aging. Among the 49 elements that were analyzed, the ones of most interest are iron (Fe), sulphur (S), calcium (Ca) and phosphorus (P). The concentrations of these ions in the ink and the paper show the effectiveness of either the removal or retention of the ink components, and the phytate reserve in the ink.[19,51] The results are shown in **Figures 6-9**.

Iron Content in Paper and Ink

Iron was detected primarily in the ink but also in the paper (**Figure 6**). There was a small amount of iron detected in the paper that did not originate from the ink, but that was possibly from the manufacturing process. This concentration of iron in the paper was not altered by any of the experimental treatments. The iron concentration in the ink was reduced by immersion in the treatment solutions. The reduction was greatest in alkaline washing alone. The higher the ratio of ethanol in the calcium phytate solution, the higher the level of iron.

The calcium phytate treatments resulted in less removal of soluble iron, since phytate complexes the Fe(II) ions and keeps them in the ink in that form. Analysis showed that alkaline water washing before treatment with calcium phytate removes more iron than without washing. It is notable that more iron is retained in the ink with ethanol modified treatments; the higher the ratio of ethanol, the more iron ions are retained. Ethanol modified phytate solutions are composed of less water, and this reduces their ability to remove Fe(II) ions.

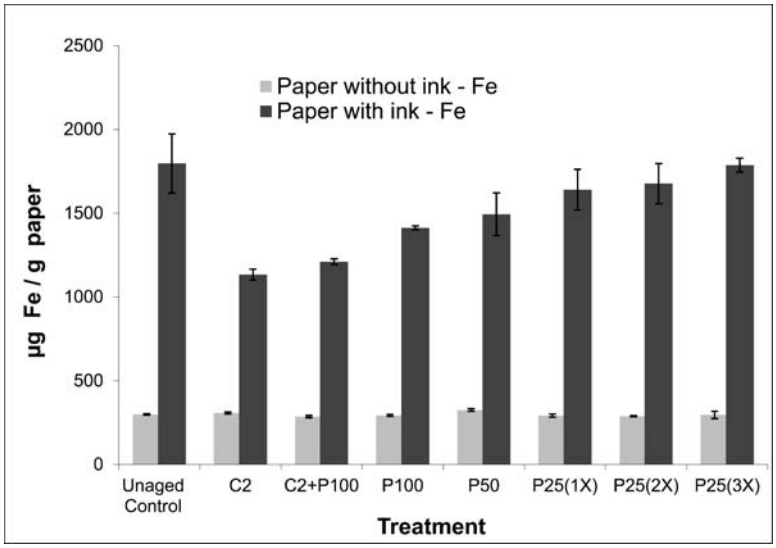

Figure 6. ICP-AES analysis of paper with and without ink after heat aging – Iron.

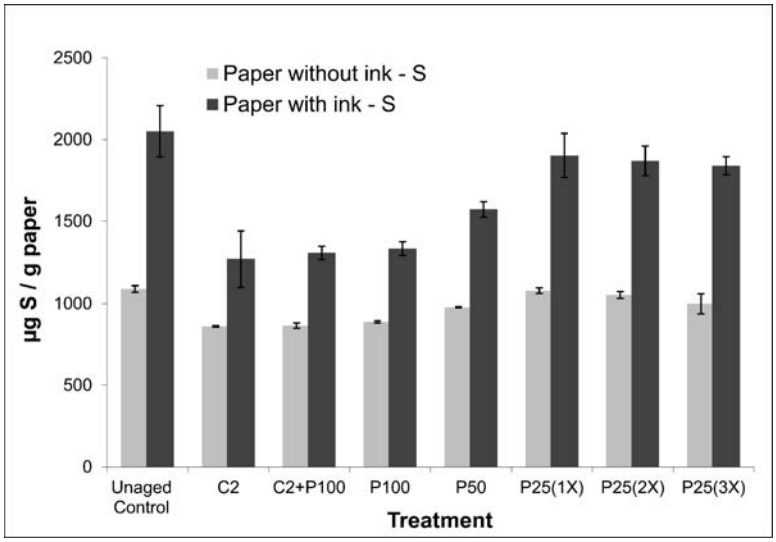

Figure 7. ICP-AES analysis of paper with and without ink after heat aging – Sulphur.

Sulphur Content in Paper and Ink

Sulphur was detected in both ink and paper (**Figure 7**). The sources of sulphur in the paper were likely calcium sulphate ($CaSO_4$) filler and alum ($Al_2(SO_4)_3.\sim14H_2O$; papermaker's alum). The presence of aluminum (approximately 500-600 µg/g) in the paper suggests the presence of alum. Sulphur levels in the paper were not very different regardless of treatment although slightly lower in C2, C2+P100 and P100 samples.

In the ink, the source of sulphur was mainly sulphate from excess iron sulphate, and sulphuric acid, a byproduct of the formation of the ink complex. Both are very water soluble. The difference between the sulphur content of paper with and without ink may indicate the sulphur content of the ink. Sulphur content varied depending on the experimental treatment. Levels were lowest in those samples treated with aqueous solutions (C2, C2+P100 and P100). Levels in samples treated with 25% ethanol modified calcium phytate were similar to that of the untreated control. The level in P50 samples was between these two groups.

The results suggest that aqueous treatments (C2, C2+P100 and P100) are equally effective in reducing the sulphur content in both the paper and the ink. Compared to the sulphur in the paper, the sulphur in the ink was much more water soluble, and more was removed by the aqueous treatments. The aluminum content of the paper was not changed by the aqueous treatments, suggesting that if it was present as alum, it was not in a very water soluble form, and that any sulphur removed from the paper did not come from alum. The addition of ethanol reduced the amount of sulphur that was removed, particularly in the inked areas of the samples; the more ethanol in the solution, the less effective it was in removing sulphur. Interestingly, the pattern of removal of iron and sulphur by each of the seven treatment variations is similar.

Calcium Content in Paper and Ink

Calcium was detected in both ink and paper (**Figure 8**). The ICP-AES results of the untreated control (C1) showed that the sample paper had a high concentration of calcium (800 µg Ca/g paper). Alkaline washing alone (C2) reduced the calcium concentration in the paper by 75%. Before the calcium phytate treatment, the main source of calcium in this paper was believed to be fillers such as calcium sulphate. The presence of calcium carbonate was considered unlikely due to the acidic nature of the paper (pH of 4.6) as the presence of calcium carbonate would give the paper an alkaline pH. In addition, the substantial loss of calcium during washing alone suggests that the form of calcium in the paper was quite soluble and is therefore not likely the result of the presence of calcium carbonate, which is quite insoluble in water at room temperature.

All of the calcium phytate treated inks showed substantially higher concentrations of calcium than the untreated control in the following order:

P100 > C2+P100 ≈ P50 ≈ P25(3X) > P25(2X) ≈ P25

The 100% phytate treatment without alkaline washing (P100) in particular increased the quantity of calcium in the ink area significantly: the quantity was substantially higher than in the paper alone. The increase in calcium in the ink indicates the amount of calcium phytate involved in complexing the Fe(II) ions in the ink.

Phosphorus Content in Paper and Ink

Phosphorus was primarily identified in samples treated with calcium phytate (**Figure 9**). Both untreated (C1) and alkaline wash controls (C2) had very little phosphorus. The concentration of phosphorus is an indicator of the quantity of phytate in the ink and the paper.[19,51] The results show that all phytate treatments successfully left behind a deposit of phosphorus. Except for alkaline wash followed by phytate, the ink areas of samples treated with phytate had substantially higher concentrations of phosphorus than did the paper. This was attributed to the complexation of the Fe(II) ions in the ink by the phytate.

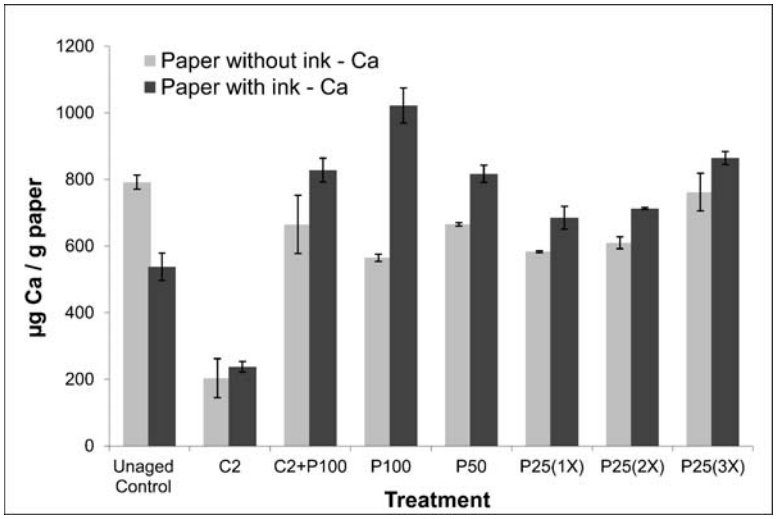

Figure 8. ICP-AES analysis of paper with and without ink after heat aging – Calcium.

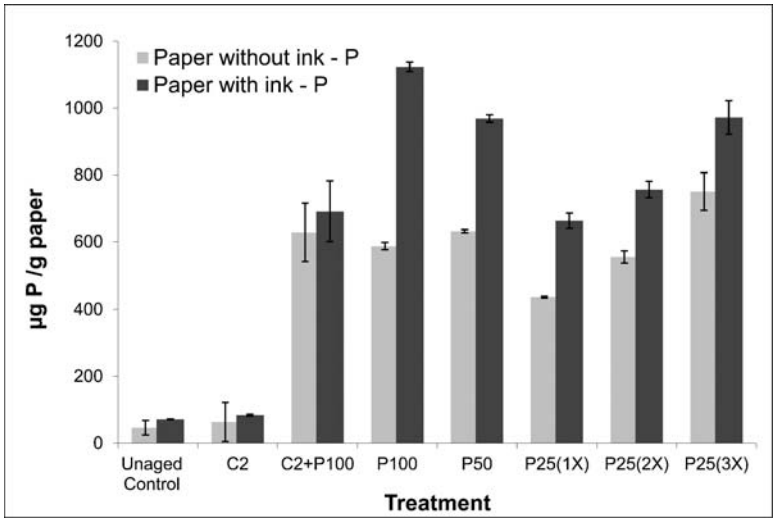

Figure 9. ICP-AES analysis of paper with and without ink after heat aging – Phosphorus.

Similar to the calcium concentrations, the deposition of phytate in the ink is ranked from greater to lesser in the following order:

P100 > P50 ≈ P25(3X) > P25(2X) > C2+P100 ≈ P25

The increase in phosphorus concentrations from P25 to P25(3X) suggests that cumulative deposition of phytate in the ink and paper took place with repeated treatments. The phytate treatments performed with alkaline washing (C2+P100) resulted in much less phosphorus deposited than without alkaline washing (P100), probably because a lot of the soluble Fe(II) ions were removed by alkaline washing alone, and were not available for complexation with the phytate.

Comparison of the ICP-AES analysis results for the 100% aqueous phytate treatments with and without alkaline washing indicates how the alkaline washing step may affect documents inscribed with iron gall ink. Concentrations of calcium, phosphorus and iron were higher on the P100 samples (no alkaline washing) but concentrations of sulphur were approximately the same on both the washed and unwashed groups of samples. This suggests that washing in an alkaline bath removes a larger percentage of water soluble iron ions, leaving fewer ions available for phytate complexation. The difference in duration of immersion of the samples in the calcium phytate is not believed to have affected the quantity of phosphorus deposited on them. Although C2+P100 samples were immersed for half as long as P100 samples (15 as opposed to 30 minutes), similar amounts of phosphorus were deposited on the paper in each case. Thus the large difference in the amount of phytate measured on the ink must be due to differences in the degree of phytate complexation in the ink rather than deposition on it due to longer immersion time.

Given current understanding of iron gall ink degradation, calcium phytate treatments that result in the greatest sulphur reduction (removal of sulphate and sulphuric acid) and the most phosphorus deposited in the ink should offer the most protection. The following three experimental treatments were therefore the most effective:

P100: phytate, no alkaline washing; one of three treatments with the least sulphur remaining and the treatment with the greatest phosphorus deposit

C2+P100: phytate with alkaline washing; one of the three treatments with the least sulphur remaining, like P100, but with a lower phosphorus deposit than P100 and P50

P50: 50:50 phytate:ethanol; more sulphur than C2+P100 and P100 and a phosphorus deposit that was less than P100 and more than C2+P100

Cold Extraction pH

The pH of the paper used in this study prior to experimental treatment was 4.6. The pH results after aging are summarized in **Figure 10**. While this sample paper was strong and still flexible, it was acidic (pH 4.2), and the ink made it more acidic (pH 3.5). Alkaline washing alone (C2) increased the pH of paper with ink from 3.5 to 4. Immersion of the samples in 100% phytate, both with and without alkaline washing (C2+P100 and P100), increased the pH of both the paper and the paper with ink (paper: 4.8; ink: 4.6) more than alkaline washing alone (C2). Immersion in ethanol modified calcium phytate increased the pH of both the paper and the paper with ink to intermediate degrees. The ranking of the solutions from the greatest to the least increase in pH in the paper with and without ink was in the following order:

P100 ≈ C2+P100 > P50 > P25(3X) ≈ P25(2X) > P25 ≈ C2 > C1

The differences in pH are attributed to the ability of a treatment solution to remove acids from the paper. Alkaline washing alone (C2) was not effective in removing acid from the

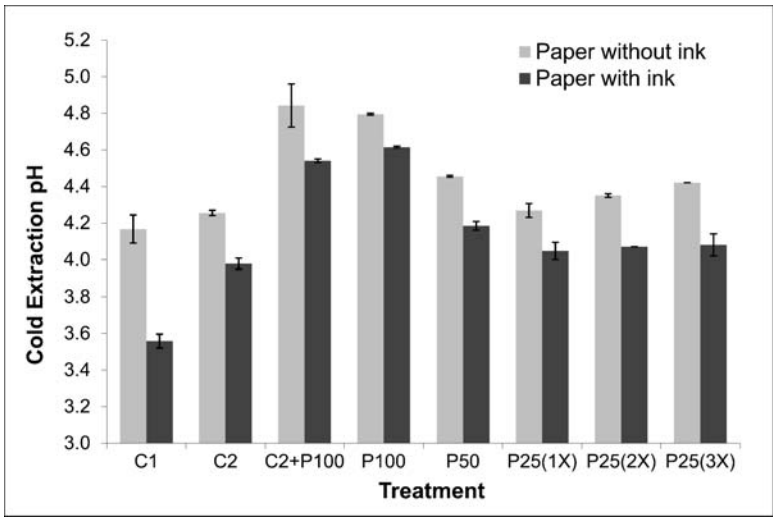

Figure 10. pH of paper with and without ink after heat aging.

Table III. Zero-span Tensile Strength of Unaged Control and Heat-aged Papers with and without Ink.

Code	Treatment Solutions	Zero-span Tensile Strength (kg/15mm; at 552 kPa (80 psi) clamping pressure)			
		Paper only		Paper with ink	
		Average	Standard Dev.	Average	Standard Dev.
C1	Untreated - Before aging	19.88	0.60	18.83	0.75
C1	Untreated - After aging	9.62	0.93	1.58	0.67
C2	Alkaline Wash	9.11	0.74	4.73	0.06
C2+P100	Alkaline Wash+100% Phytate	13.24	0.79	10.42	0.81
P100	100% Phytate	13.85	0.54	11.48	0.63
P50	50:50 Phytate:ethanol	12.19	0.57	8.34	0.74
P25	25:75 Phytate:ethanol	11.16	0.89	4.89	1.62
P25(2X)	25:75 Phytate:ethanol (2X)	11.51	0.68	4.83	0.97
P25(3X)	25:75 Phytate:ethanol (3X)	9.76	0.74	3.63	1.08

paper. Therefore the pH increase (paper without ink from 4.2 to 4.8; paper with ink from 3.5 to 4.6) in the samples treated with 100% calcium phytate (C2+P100 and P100) can be attributed to the phytate treatment. The addition of ethanol to the phytate solution reduced the concentration of phytate and accordingly its effectiveness in removing acids from both the paper with and without ink.

A somewhat unexpected result was that alkaline water (pH 8.5) washing was less effective in increasing the pH of ink and paper than was the calcium phytate solution (pH 5.8). The ineffectiveness of the alkaline water in neutralizing and removing acids from paper and ink may be due to a low concentration of hydroxide ions (approximately 0.003 mM). Calcium phytate solutions, being higher in concentration (1.75 mM), have higher ionic strength, and are thus more effective in solubilizing acids by ionic exchange.

Zero-span Tensile Strength

The zero-span tensile strength results are summarized in **Table III**, and the percent retention in **Figure 11**. The percent retention of zero-span tensile strength after heat aging is calculated relative to the untreated control (C1) before heat aging. After heat aging, all papers with and without ink decreased in strength. Due to the acidity of the ink, paper with ink lost more strength than paper alone.

The retention of zero-span tensile strength varied with experimental treatment and can be ranked from higher to lower in the following order:

P100 ≈ C2+P100 > P50 > P25 ≈ P25(2X) ≈ C2 > P25(3X) > C1

Alkaline washing alone (C2) did not benefit the paper without ink noticeably, but paper with ink showed significantly greater retention in zero-span tensile strength. Aqueous phytate treatments (C2+P100 and P100) resulted in the greatest retention of zero-span tensile strength for the paper both with and without ink, but the degree of benefit for paper with ink was much greater. Samples treated with ethanol modified calcium phytate exhibited less zero-span tensile strength retention, particularly with the more dilute solutions. The degree of retention is similar for the P25, P25(2X) and P25(3X) treatments. Strength retention may be because of a combination of acid removal and chelation of Fe(II) ions from the ink.

The zero-span tensile strength test measures average fibre strength, an important factor in determining paper strength. The results have been shown to have good correlation with viscometric degree of polymerization (DPv, a measure of polymer chain length) for paper made from pure cellulose,[52] and also with averaged molecular weight of different types of paper.[53] For papers that are in advance stages of deterioration, but prior to reaching a "leveling-off degree of polymerization," zero-span tensile strength is found to be more sensitive to change than molecular weight analyses.[53] In this study, zero-span tensile strength was used as a measure of the effectiveness of the experimental treatments in retaining the fibre strength of the paper with and without ink.

The correlation between the zero-span tensile strength results and the pH of the paper is notable: the higher the pH, the greater the retention of zero-span tensile strength (**Figure 12**). No correlation between zero-span tensile strength and calcium or phosphorus concentrations was found. The pH of paper is an important determinant of its chemical stability.[12,54,55] At pH

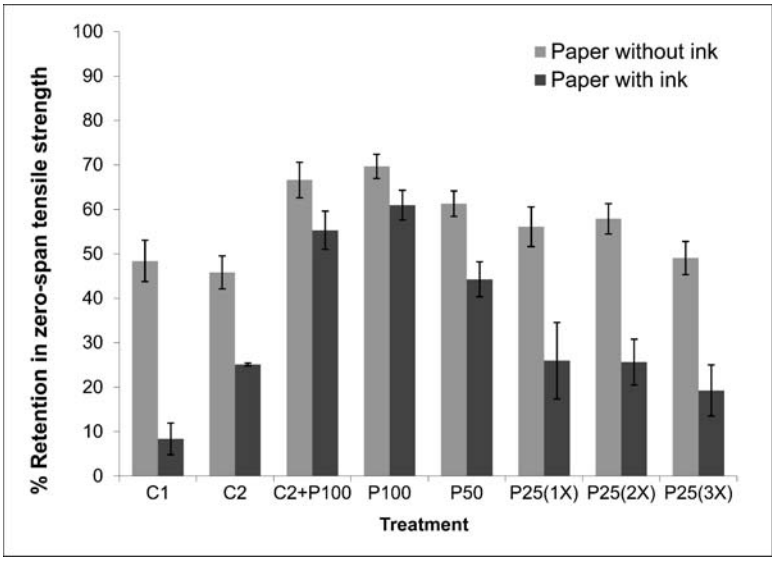

Figure 11. Percent retention of zero-span tensile strength (mean and standard deviation) after heat aging of paper with and without ink.

below 7, the rate of cellulose degradation is pH dependent: the lower the pH the higher the rate.[56] The correlation of zero-span tensile strength with pH but not with indicators of calcium phytate complexation in this study confirms that when the paper is acidic (below pH 6), the pH of the paper, and not the presence of phytate, is the dominant factor in determining its rate of deterioration.[56] This does not negate the benefit of calcium phytate, which is in delaying the regeneration of Fe(II) in inks, but it does show that oxidation catalyzed by Fe(II) is not the dominant degradation process occurring in papers that have an acidic pH.

Summary and Conclusions

The degradation of paper by iron gall ink is attributed to two main pathways: hydrolysis, catalyzed by acids, and oxidation, catalyzed by metal ions such as Fe(II) ions. At an acidic pH (below 6), hydrolysis is the predominant reaction and the rate of paper deterioration is a function of pH: the lower the pH, the higher the rate of deterioration.[56] Aqueous phytate-bicarbonate combats this deterioration by removing both catalysts: acids and Fe(II) ions. Water partially solubilizes and removes both acids and Fe(II) ions; phytate, as an antioxidant, removes excess Fe(II) ions by chelation, and bicarbonate neutralizes any remaining acids and provides a buffer reserve.

Effectiveness of Ethanol Modified Phytate without Deacidification

In the conventional phytate treatment of iron gall inks, deacidification is an essential component. However, for research purposes, this study aimed to isolate the benefits of calcium phytate. For these ink samples, excess Fe(II) ions were mitigated by phytate complexation, but the acids in the ink and paper were mitigated only by solubilization and partial neutralization by the phytate solution (pH 5.8).

Since ethanol diluted solutions contain less water/phytate, they are less effective in solubilizing acids, and are thus expected to be less effective on their own in protecting paper from degradation by hydrolysis during heat aging. As an indicator of the overall protection for paper inscribed with iron gall ink, the results for retention of zero-span tensile strength after heat aging support this hypothesis. Comparing the effectiveness of the seven treatment variations, the ranking from the most effective to the least effective solution is as follows:

P100 ≈ C2+P100 > P50 > P25 ≈ P25(2X) ≈ C2 > P25(3X) > C1 (no treatment)

As one would expect, undiluted calcium phytate, with or without alkaline washing, offered the best protection for paper with ink. Alkaline washing (C2+P100) removed slightly more Fe(II) ions compared to no alkaline washing (P100), but it did not remove more acid. The two groups of samples had similar pH and tensile strength after aging. Alkaline washing did not have any benefits over no alkaline washing. While diluting phytate solutions with ethanol lowers their effectiveness as compared to 100% phytate, the diluted solutions still offer some protection over no treatment at all even when diluted to 75% ethanol (P25).

Effectiveness of Repeated Applications of Ethanol Modified Phytate

Most conservators would understandably be reluctant to treat an object inscribed with slightly soluble ink with multiple immersion treatments, due to both the risk of ink migration and the stress on the paper from handling and drying between applications. There may, however, be exceptional circumstances under which repeated applications of ethanol diluted calcium phytate – possibly on a suction table – might be considered, and as such it is worth reporting that repeated applications result in the accumulation of more phytate, and thereby offer more protection against the recurrence of Fe(II) ions.

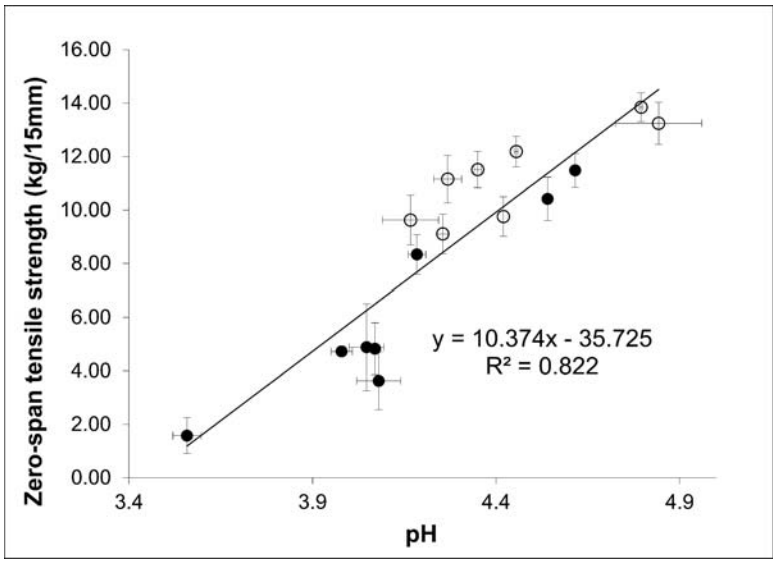

Figure 12. Correlation between zero-span tensile strength and pH of paper after heat aging.

The results of elemental analyses (ICP-AES) showed that repeated treatment with P25 increased the deposition of calcium and phosphorus on the samples. There were significantly higher concentrations of calcium and phosphorus on the ink areas where Fe(II) ions were available for complexation with phytate, than on the surrounding paper. Bathophenanthroline test results after heat aging showed that an increase in the deposition of phytate results in a delay in the recurrence of Fe(II) ions. Although that alone does not correspond to a greater retention of zero-span tensile strength after aging, it does indicate that multiple applications of fresh ethanol modified phytate solutions have benefit.

Necessity of the Deacidification Treatment Step

The results of the analyses showed that each of the ethanol modified calcium phytate treatment variations, without deacidification, were able to increase the retention of the paper's strength to varying degrees after heat aging. The determining factor in the reduced effectiveness of the ethanol modified phytate treatments versus 100% phytate was *not* the lack of deposition of calcium phytate, but rather their *reduced efficiency in removing acids,* as evidenced by the lower pH among these samples. While calcium phytate can benefit paper inscribed with iron gall ink, alone it is not sufficient: it must be followed by subsequent deacidification, such as with ethanol modified calcium carbonate.[18] The results of this study suggest, therefore, that as long as it is followed by deacidification, ethanol modified calcium phytate may be an effective treatment option. Further testing of the complete treatment is required to confirm this hypothesis.

Elimination of Alkaline Water Washing

The risk of lateral migration (bleeding) of some iron gall inks in high humidity environments or during water washing is well documented.[6,14,27,30,36,57] Alkaline water washing before the application of calcium phytate is a common treatment step, because it helps remove acids, excess Fe(II) ions and some of the degradation products that cause paper discolouration.

For inks containing large quantities of excess Fe(II) ions, the alkaline washing step risks the migration of these ions during the drying process prior to calcium phytate treatment. UV illumination of samples from research carried out by the CCI and Library and Archives Canada, showed that inks containing a large excess of Fe(II) ions (i.e. those that test very positive with the use of bathophenanthroline test papers, Fe(II)>50) showed the most extensive lateral migration of ink components when exposed to high humidity and when washed in aqueous solutions without phytate; whereas inks treated with phytate did not suffer from lateral migration after treatment or when exposed to high humidity conditions.[36]

Jembrih-Simbürger et al.,[15] Choi and Zinsmeister,[33] and Downey[44] have investigated the possibility of eliminating the alkaline washing step and placing the inked document directly in a phytate solution. This allows the immediate chelation of Fe(II) ions to occur. Since the Fe-phytate complex is much less water soluble compared to Fe(II) ions, this greatly reduces the risk of lateral migration of Fe (II) ions during the drying process.

After the same duration of immersion (30 minutes in 100% phytate as opposed to 15 minutes in alkaline water followed by 15 minutes in 100% phytate), the pH results from this study showed that the same amount of acids are being removed in a phytate treatment whether the inked paper was washed in alkaline water or not. The zero-span tensile strength results showed that both treatment variations offer the same degree of protection, meaning that eliminating the alkaline washing step does not diminish the effectiveness of the phytate treatment. The only difference between the two variations is that without alkaline washing, more Fe(II) ions are retained in the ink, and consequently more phytate is deposited in the ink during treatment. These results indicate that the necessary removal of the alkaline washing step from the treatment of documents inscribed with slightly soluble iron gall ink does not diminish the effectiveness of ethanol modified calcium phytate treatments. Furthermore, the results suggest that the alkaline washing step might be eliminated from the calcium phytate treatment protocol for *all* iron gall ink inscribed documents.

Materials

Ammonium hydroxide (9721-02, 28-30%; 500mL) certified A.C.S.: J.T. Baker, Mallinckrodt Baker Inc., distributed by Alphachem Ltd., Milltower Court, Mississauga, Ontario L5N 5Z6, Canada; Tel.: 905-821-2995; Fax: 905-821-2660; Website: <http://www.alphachem.ca/>

Bathophenanthroline indicator paper for iron ions: Preservation Equipment Ltd, Vinces Road, Diss, Norfolk, IP22 4HQ, UK; Tel.: 44 1379 647400; Fax: 44 1379 650582, <www.preservationequipment.com> or University Products of Canada (Catalogue No. 539-3000), BFB Sales, 2957 Inlake Court, Mississauga, Ontario L5N 2A4, Canada; Tel.: 905-858-7888; Fax: 905-858-8586

Calcium carbonate powder (1288-01; 500g) certified A.C.S.: J.T. Baker, Mallinckrodt Baker Inc. (as above)

Calcium hydroxide powder (1372-01; 500g) certified A.C.S.: J.T. Baker, Mallinckrodt Baker Inc. (as above)

Color chart for bathophenanthroline indicator paper: Canadian Conservation Institute, 1030 Innes Road, Ottawa, Ontario K1A 0M5, Canada; contact: season.tse@pch.gc.ca

Ethanol (Anhydrous ethyl ethanol, 500ml): Commercial Alcohols Inc., 2 Chelsea Lane, Brampton, Ontario L6T3Y4, Canada; Tel.: 905-790-7500; Fax: 905-790-7700; Website: <http://www.comalc.com/>

Ferrous sulfate hepta-hydrate (I146-500) certified A.C.S.: Fisher Scientific Limited, 112 Colonnade Road, Ottawa, Ontario K2E 7L6, Canada; Tel.: 613-226-8874; Fax: 613-226-8639; Website: <www.thermofisher.com>

Gum arabic (acacia powder; G85; 453g, laboratory grade): Fisher Scientific Limited (as above)

Hybridization tubes with polypropylene screw cap and a Teflon

gasket (Lab-Line No.308-9): Discontinued. Alternatives are available from Fisher Scientific Limited (as above)

Phytic acid (40%, 1L, 28966-3): Sigma-Aldrich Canada Ltd., 2149 Winston Park Drive, Oakville, Ontario L6H 6J8, Canada; Tel.: 800-565-1400; Fax: 800-265-3858; E-mail: canada@sial.com; Website: <www.sigmaaldrich.com>

Tannic acid (30337): VWR International (formerly BDH Chemicals Ltd.), 2360 Argentia Road, Mississauga, Ontario L5N 5Z7, Canada; Tel.: 800-932-5000; Fax: 800-668-6348; Website: <https://us.vwr.com>

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