

FULL PAPER

STABILISATION OF IRON GALL INK: AQUEOUS TREATMENT WITH MAGNESIUM PHYTATE

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Corrosive iron ions and acids in iron gall inks lead to enhanced degradation of paper. Several conservation practices have been used to stabilise endangered documents in the past centuries. The most effective aqueous stabilisation method developed to date is the so called “Calcium phytate” method. In this contribution we demonstrate that a treatment using magnesium phytate is equally effective, while additionally exhibiting several advantages. Due to the higher solubility of magnesium phytate compared to calcium phytate, it is not required to add an aqueous solution of ammonia, which poses several health risks.

It is also shown that in order to optimise the efficiency of treatment, the pH of magnesium or calcium phytate solution should be adjusted to 5.8-6.0.

1 Introduction

Cellulose is one of nature's more durable organic materials if stored at suitable conditions. This has been attested by numerous archaeological textiles, which endured the test of time for more than two millennia. Yet certain compounds, such as acids and transition metal ions, which are present in historical iron gall inks, dramatically reduce its stability, resulting in the loss of its mechanical properties. Unfortunately, iron gall ink, the most widely used ink from the Middle ages up to the 20th century, contains both corrosive transition metals and acids, and may thus inflict severe damage to paper.¹

For several centuries, iron gall ink induced decay, referred to as ink corrosion, has been acknowledged as one of the major threats to the written cultural heritage. As early as 1765, the English chemist William Lewis published a treatise on the stability of iron gall inks and in 1898, the first conference was held in the city of Sankt Gallen in Switzerland.²

Several conservation practices have been used to stabilise endangered documents through the centuries.^{3,4} The most effective aqueous

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ous stabilisation method developed to date is the so called "Calcium phytate" method, which involves inhibition of oxidative decay with complexing agent *myo*-inositol hexaphosphate (phytate) and subsequent deacidification using an aqueous solution of calcium bicarbonate. The use of phytate for stabilisation of iron gall inks was first proposed by Han Neevel in 1995.⁵ Due to the use of alkaline phytate acid dodecasodium salt, paper yellowing was observed. To overcome this, sodium hydroxide was replaced by calcium carbonate. As the solubility of calcium phytate is quite low at pH above 5, ammonia was added to raise the pH of the aqueous solution to the recommended 5.0-5.8.^{6,7} Since then, the method has been developed into a conservation treatment⁸⁻¹⁰ and several researchers have so far shown its beneficial effect on the stability of paper containing iron gall ink.¹¹⁻¹⁷ Since July 2007, a detailed description of the proposed phytate treatment is available.¹⁸ While the treatment presents a significant advance in stabilisation of iron gall ink, there is still room for improvement, in view of which our present research focuses on the following:

- pH of the phytate solution has been set quite broadly (5.2-5.8),
- solubility of calcium phytate decreases as the pH approaches 5.8, which is demonstrated by its precipitation. Most of the "treatment solutions" are in fact suspensions and may lead to inhomogeneous deposits on the surface of the objects,¹¹
- it requires the use of aqueous solution of ammonia. According to the "Risk and Safety statements" (also known as R/S statements, R/S numbers, R/S phrases, and R/S sentences)¹⁹ aqueous ammonia solutions may cause severe burns, may irritate eyes, skin and respiratory system, pose danger of very serious side effects, including serious damage to eyes, may cause cancer etc. On the other hand, phytic acid is described as irritating to eyes, respiratory system and skin. In the preparation of solutions for conservation, one should avoid the use of unsafe or environmentally unfriendly chemicals.

The objective of our research project is to offer an alternative phytate treatment, which would overcome some of the discussed shortcomings.

2 Experimental

The following papers were used for the study:

- Whatman paper no.1 (Maidstone, UK, 86.0 g m⁻², degree of polymerisation (DP): 2630 ± 20).
- Rag paper. Several 19th-century books made from cotton fibres and sized with alum/gelatine sizing were selected. Book blocks were trimmed on all three edges by 2 mm. The unprinted sections

were then collected and the fibres were suspended in cold water for 24 h. From these historical rag fibres, standard test sheets were produced²⁰ (DP: 730 ± 30).

Ink used in the study was produced by dissolving the following components in 0.1 L of deionised water: 3.14 g of gum arabic, 9.84 g of tannin (puro, Carlo Erba), 8.34 g of FeSO₄ × 7H₂O (Riedel-de Haën).

Selected ink was applied to the paper using a Roland DXY plotter, with the pen 0.6 mm in diameter at a speed of 3 cm s⁻¹.

The papers containing the ink were pre-aged at 70 °C and 65% relative humidity for 24 h. After the treatment, the paper were exposed to 80 °C and 65% RH for up to 11 days.

The following treatments were evaluated:

- "Calcium phytate" treatment (CaPhy):

Phytate solution was prepared according to the ICN recipe.²¹ To 2.88 g of 40% (w/w) phytic acid solution, 0.44 g of CaCO₃ was added, after which the solution was diluted to 1 L with deionised water. Diluted ammonia solution (1.25% V/V) was added to reach the desired pH. The paper (3 g of paper per 1 L of solution) was immersed into the phytate solution for 15-20 min, after which it was deacidified by immersion into two consecutive baths of 0.01 mol L⁻¹ Ca(HCO₃)₂ for 20 min.

- "Magnesium phytate" treatment (MgPhy):

2.88 g of 40% (w/w) phytic acid was added to 1 L of deionised water. 0.2 g of MgCO₃ (Riedel-de Haën) was added and the solution stirred dissolved until the desired pH (4-6.5) was reached. This may take several hours. The solution was filtered. pH of the final solution was determined again prior to the treatment. The paper (3 g of paper per 1 L of solution) was immersed into the phytate solution for 15 min, after which it was deacidified by immersion into two consecutive baths of 0.01 mol L⁻¹ Ca(HCO₃)₂ for 20 min.

- Deacidification by immersion in aqueous solution of Ca(HCO₃)₂:

Deacidification was performed by immersing the sample into two consecutive baths containing 0.01 mol L⁻¹ of Ca(HCO₃)₂ for 20 min (3 g of paper per 1 L of solution).

Samples containing iron gall ink were then subjected to accelerated degradation at 80 °C and 65% RH in a Vötsch VC 0020 ageing oven (Vötsch Industrietechnik, Balingen-Frommern, DE).

The standard viscometric method was used (ISO 5351/1)²² to determine DP of the cellulosic fraction of paper.

DP was calculated from intrinsic viscosity using the Mark-Houwink-Sakurada equation:²³

$$DP^{0.85} = 1.1 \times [\eta]$$

Iron content in paper was determined using atomic absorption spectroscopy. Determination of the metal content using AAS was performed after microwave-assisted wet digestion of samples (~5 mg) in PTFE digestion vessels (CEM MDS-2000, Matthews, NC), using 5 mL of 20% (w/w) aqueous solution of nitric acid. The digested samples were subsequently transferred to measuring flasks and metal content was determined using flame AAS (Perkin-Elmer 1100B, Boston, MA). This procedure was repeated three times and the standard deviation of the three independent determinations was calculated.

CIE L*a*b* colour coordinates were determined relative to Minolta polymeric standard using Minolta CM-3610d spectrometer.

Determination of pH of the paper extract was performed in the following way: to 20-50 µg of sample, 5 µL of deionized water was added and left overnight. pH was determined in the extract using a micro-combined-glass electrode (MI 4152, Microelectrodes, Bedford, NH).

3 Results

According to the instructions,²¹ pH of the calcium phytate treatment solution should be between 5.0-5.8. Another reference recommends that the pH of the solution is between 5.2-5.8.¹⁸ However, our earlier research suggested, that pH of the treatment solution has a significant effect on the stability of iron gall ink containing paper. Model samples treated with the phytate solution at pH 5.0 degraded 2-4 times faster than those treated with a phytate solution at pH 6.2.¹⁴ We therefore decided to evaluate the effects of calcium and magnesium phytate solutions at a variety of pH values (Figure 1).

The results presented in Figure 1 demonstrate that the optimum pH of calcium and magnesium phytate solutions is between 5.8 and 6.0. Also, calcium and magnesium phytate solutions, when used in this pH interval, stabilise paper to a similar extent. While CaPhy treatment results in paper, which is 12 ± 2 times more stable than the untreated control, this factor of stabilisation is 12.8 ± 0.7 in case of MgPhy, demonstrating that there is no significant difference in their effectiveness.

This is probably due to the fact that both treatments resulted in the removal of similar amounts

of iron from paper; (44 ± 2)% in case of CaPhy and (41.9 ± 0.6)% in case of MgPhy (Figure 2).

A similar observation regarding the effect of the two phytate solutions can be made when rag paper with iron gall ink is treated using either of the two phytate solutions at pH 6 (Figure 3). Paper, treated with calcium phytate is more stable than the untreated one by a factor of 3.8 ± 0.2 , while the magnesium analogue prolongs its lifespan by a factor of 4.1 ± 0.5 , at 80 °C and 65% RH.

Aqueous treatment of paper with iron gall inks with magnesium bicarbonate has received some ill reputation in the recent years, as it had been demonstrated, that it causes yellowing of certain model papers made from cellulose pulps²⁴ and fading of some iron gall inks.²⁵ The authors proposed that both effects are caused by high pH values, which may result from such treatment.

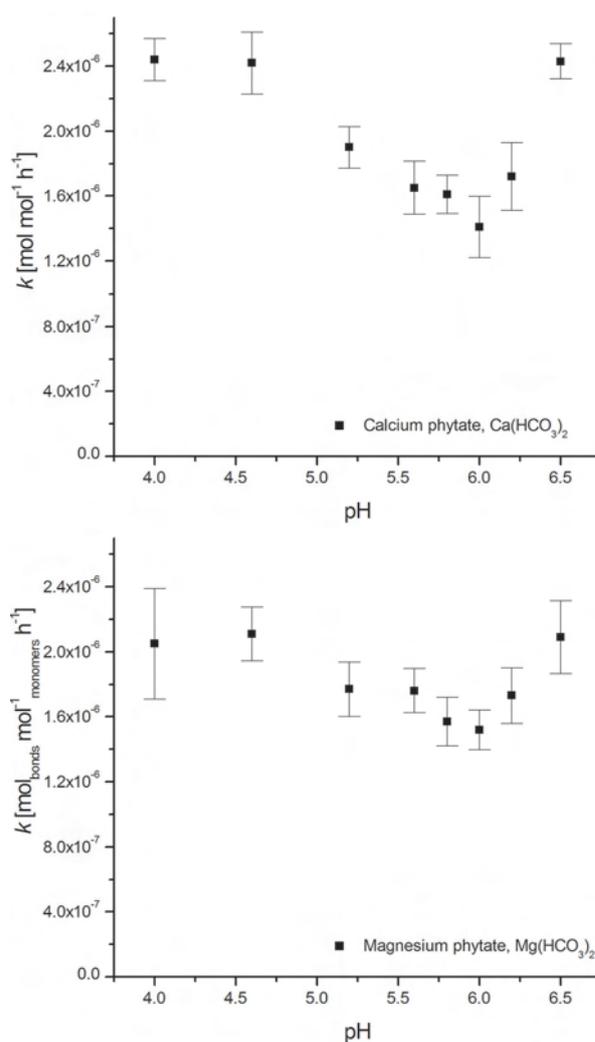


Figure 1: Rate constants of cellulose chain scission in Whatman paper containing iron gall ink, treated with solution of calcium (above) and magnesium (below) phytate and deacidified using calcium bicarbonate, at 80 °C, 65% RH.

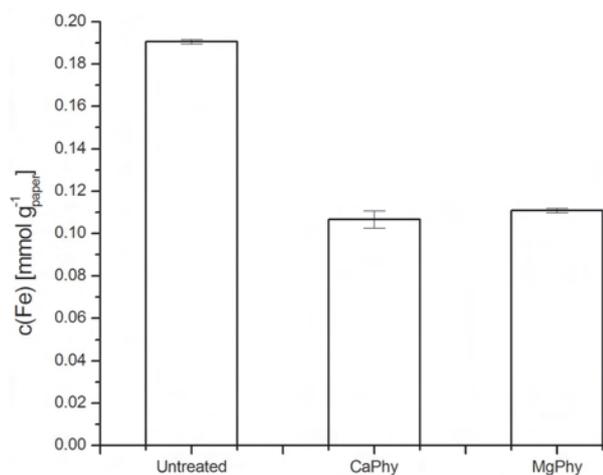


Figure 2: Content of iron in Whatman paper with iron gall ink, either untreated, or treated with solutions of calcium (CaPhy) or magnesium (MgPhy) phytate at pH 6.0 and deacidified using calcium bicarbonate.

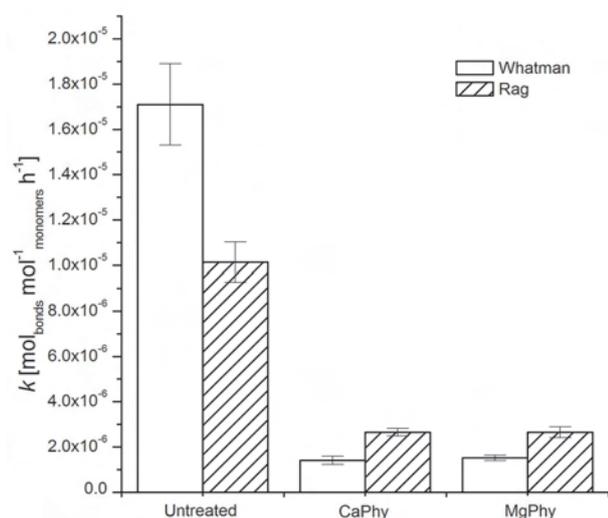


Figure 3: Rate constants of cellulose chain scission in Whatman and rag papers containing iron gall ink, either untreated or treated with solutions of calcium (CaPhy) or magnesium (MgPhy) phytate at pH 6.0 and deacidified using calcium bicarbonate, at 80 °C, 65% RH.

	0 h	184 h
	pH	pH
Untreated	3.75 ± 0.04	2.71 ± 0.09
CaPhy	7.28 ± 0.08	6.98 ± 0.08
MgPhy	7.0 ± 0.1	6.9 ± 0.1

Table 1: pH of Whatman paper with iron gall ink, either untreated or treated with solution of calcium (CaPhy) or magnesium (MgPhy) phytate and deacidified using calcium bicarbonate. pH was determined before (0 h) and after 184 h of accelerated degradation at 80 °C and 65% RH.

It is important to stress that the risk of ink and paper discolouration, which was observed when iron gall inks were deacidified using Mg(HCO₃)₂, does not exist in the case of MgPhy treatment. The resulting pH is similar, regardless of whether CaPhy or MgPhy process is used (Table 1).

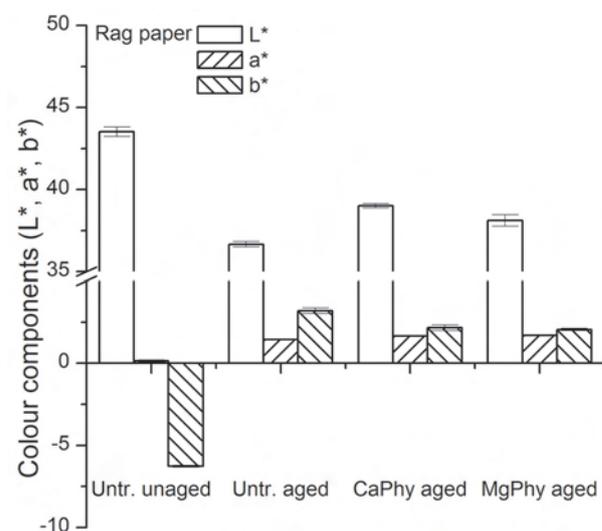
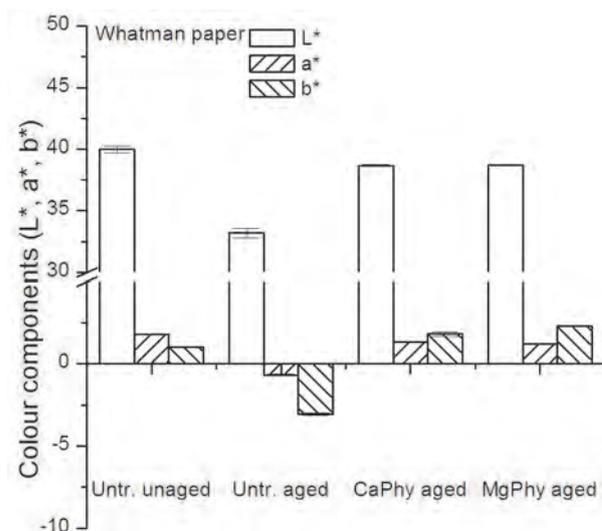


Figure 4: L*, a* and b* values of untreated paper with iron gall ink before ageing (untr. unaged) and after ageing (184 h, 80 °C, 65% RH) for untreated (untr. aged) paper, or treated with calcium (CaPhy aged) or magnesium phytate (MgPhy aged) and deacidified with using calcium bicarbonate.

Nevertheless, we have also decided to evaluate the effects that the treatments may exert on colour of the ink during accelerated degradation.

The most often used system for colour evaluation is CIE L*a*b*, proposed by Commission Internationale de L'Éclairage in 1976, which allows the specification of colour perception in terms of three-dimensional space. The L*-axis is known as the lightness and extends from 0 (black) to 100 (white). The other two coordinates, a* and b*, represent redness-greenness and yellowness-blueness, respectively.

The long-term effects of calcium and magnesium phytate treatments on L*, a* and b* values of Whatman and rag paper with iron gall ink are presented in Figure 4. As expected, changes in the b*

component are the most dramatic. This is due to the decomposition of the greyish-blue iron gall complex, during which several yellow-brown products are formed. It may also be observed that there are no significant differences in brightness (L^*) values between papers, treated with CaPhy or MgPhy methods.

4. Conclusion

The presented research demonstrates that magnesium phytate is at least equally effective in inhibiting ink corrosion as the traditionally used calcium phytate. It possesses certain advantages over the latter, most importantly. pH of the treatment solution can be raised to the desired level using MgO or $MgCO_3$ without the use of ammonia. The step involving additions of harmful aqueous solution of ammonia is avoided.

pH of the magnesium phytate solution should be adjusted by addition of an appropriate amount of $MgCO_3$ to 5.8-6.0, where the stabilising effects of treatment are optimal. To obtain a solution of magnesium phytate at pH 6, 0.16 g of $MgCO_3$ and 2.88 g of phytic acid solution (40%) are added to 1 L deionised water. The mixture is left standing for 12 h. After the reaction, a small amount of precipitate remains.

To complete the study, several historical papers will be evaluated with respect to the possible negative side effects.

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