INTRODUCTION:
CAUSES OF INK CORROSION

Ink corrosion, the degradation of the substrate caused by the corrosive action of iron gall inks, is a difficult restorative problem encountered with manuscripts and pen drawings made on paper or parchment. Different causes have been suggested for the degradative process. Iron gall inks usually contain acid: pH values range from 1.0 - 3.1\(^7\). Acid catalyses the hydrolysis of cellulose in paper\(^2\). In general, deacidification slows down ink corrosion\(^3\). During accelerated ageing however, it failed to protect the paper against the recurrence of new acidity, as was shown by Hey\(^4\). Therefore, acidity cannot be the only cause of ink corrosion. Simulating tests of ink corrosion by accelerated ageing of different types of paper treated with iron gall ink showed that the lignin-free paper degraded faster than the lignin-containing paper, even in the presence of acid alum sizing in the latter\(^5,6\). Lignin will act as an anti-oxidant because it is oxidised faster than cellulose and forms stable radicals\(^7\). Therefore, this observation is indicative of the oxidative character of the process.

Iron(II) ions are suspected to cause the oxidative degradation of cellulose by catalysing the formation of hydroxyl radicals (HO\(^-\)) from hydrogen peroxide in the so-called "Fenton reaction", as is shown below\(^7,8\).

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{HO}^- + \text{OH}^-
\]

Hydrogen peroxide is formed during the reduction of molecular oxygen by iron(II) ions. Its formation at the ink surface could be detected by the Russell test, shown in Figure 1. This test uses a sensitised black-and-white film (details given in the experimental section)\(^9,10\).

\[
\text{Fe}^{2+} + \text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + \text{HOO}^-
\]

\[
\text{Fe}^{2+} + \text{HOO}^- + \text{H}^+ \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O}_2
\]

Hydroxyl radicals are very reactive and readily abstract hydrogen from cellulose, leading to the formation of organic radicals (R\(^-\)). These react in a chain reaction with oxygen and a new cellulose molecule (R'H) to form cellulose hydroperoxide (ROOH) and a new radical (R'\(^-\)), as is shown below.

\[
\text{R}^- + \text{O}_2 \rightarrow \text{ROO}^-
\]

\[
\text{ROO}^- + \text{R}'\text{H} \rightarrow \text{ROOH} + \text{R}'.
\]

Chain scission occurs when cellulose hydroperoxide reacts with iron(II) ions in a Fenton-like fashion, as is shown in Figure 2.

Iron(II) ions thus play a dominant role in the oxidation of cellulose. Most old iron gall ink recipes contain an excess of iron(II) sulphate compared to the tannin content. According to an official advertisement of the British government of 1889, a stable black iron gall ink should not contain more than 3 parts of nutgalls to 1 part of iron(II) sulphate\(^11\). Upon ageing, this ink does not turn brown. This ideal ratio was established earlier by Caneparius in 1660 and Lewis in 1787\(^12\). Assuming a tannin content of 55% in the nutgalls, molecular weights of the tannin and iron(II) sulphate to be respectively 1700 and 278, this ratio amounts to a weight ratio of 7.3:1 for tannin to iron in the iron gall ink. This ratio falls well within the range of ratios (7 - 10:1) calculated from the weight percentages of iron and tannin given by the Merck Index for iron(III) tannate (70 - 80% tannin, 8 - 10% iron), thereby confirming these results\(^13\). A survey of 104 historical ink recipes from the 15th to the 19th century showed that the majority (about 30%) contained 2 parts of nutgalls to 1 part of iron(II) sulphate, which is equivalent to a molecular ratio of iron(II) sulphate to tannin of 5.5:1. The mean ratio was calculated to be 1.6 parts to 1\(^14,15\). Therefore, most of these recipes contain too much iron. Because of the presence of reducing substances in the
Moreover, it does not block the coordinating position scyllo-inositol hexakisphosphate with all phosphate groups in equatorial positions shows less effective blocking of the Fenton reaction. Acid also stabilises iron(II) ions by preventing them to be oxidised. The brown discolorations usually observed along the ink regions in paper artefacts damaged by ink corrosion, are indicative of the presence of iron(II) ions in the original ink. These discolorations may have been caused by the diffusion of the iron(II) ions out of the acid ink regions to less acid surroundings, where they were oxidised to less soluble iron(III) hydroxides. In this way, deacidification slows down the oxidative degradation by diminishing the amount of iron(II) ions through the oxidation to iron(III) hydroxides. At too high pH-values however (pH > 10), the ink itself can be degraded by decomplexation and oxidation of the tannin to light-coloured products.

**TREATMENT OF INK CORROSION (THEORY)**

A conservation treatment of paper artefacts threatened by ink corrosion should be based on the inhibition of the acid hydrolysis and the iron(II)-catalysed oxidation of cellulose. Attempts have been made to prevent the catalytic oxidation by complexing the iron(II) ions with Ethylene Diamine Tetra Acetate (EDTA). These were not successful; on the contrary: the addition of EDTA accelerated the degradation process during artificial ageing. This phenomenon can be explained by the fact that EDTA also complexes iron(III) ions, rendering them soluble. They can then be reduced to iron(II) ions. Moreover, it does not block the coordinating position for hydrogen peroxide at the iron(II) ion, therefore it does not prevent the formation of hydroxyl radicals by the Fenton reaction. Only a few complexing agents block the Fenton reaction. One of them is phylic acid, a natural anti-oxidant present in seeds. Mixed calcium and magnesium salts of phylic acid (phytates), store about 60 - 90% of the phosphor present in plant tissues. Cereals, nuts, legumes, spores, oil seeds, needles and pollen contain up to 5% by weight of these phytates. Phytate has been demonstrated to block the iron-catalysed oxidation of unsaturated fats. It seems very successful in protecting seed lipids against oxidation, as some seeds germinated even after 4 centuries of dry storage. The structure of phylic acid in aqueous solution is shown in Figure 3. It is the completely phosphorylated ester of myo-inositol (myo-inositol hexakisphosphate). Five of the phosphate groups are in an equatorial position relative to the cyclohexane skeleton, one is in an axial position. This sequence resembles that of the successive positions of the legs, tail and head of a turtle (Figure 3). This sequence is essential for the anti-oxidant function, as scyllo-inositol hexakisphosphate with all phosphate groups in equatorial positions shows less effective blocking of the Fenton reaction.

Before applying phytate to the conservation treatment of ink corrosion, it should be proven that the iron-gall ink itself is not destroyed by the compound. A useful parameter is the stability constant (K) of the iron(III)-phytate complex. Its value (log K = 17.63 at pH = 6) is much lower than that of the iron(III)-EDTA complex (log K = 25.1). EDTA did not destroy a black iron-gall ink, therefore phytate neither is expected to do so. Problems could arise when applying phytate to brown-coloured inks in an acid environment. These inks are expected to consist mainly of iron(III) oxyhydroxide or rust. Phylic acid is used as a rust-converting agent and the resulting product iron(III) phytate is white. The acidity is needed to dissolve the iron(III) oxyhydroxide. When using phytate under neutral or slightly alkaline conditions however, no problems are expected.

Similar to other phosphates, phytate salts act as pH-buffers in the range between pH = 4 and pH = 9. Because of this, they could also be used to deacidify the paper materials. A single treatment with phytate could therefore protect the threatened paper against the acid hydrolysis and the iron(II)-catalysed oxidation. The aim of this research project was to investigate the effects of a conservation treatment with phytate by simulating ink corrosion with accelerated ageing tests.

**EXPERIMENTAL**

**Russell test**

Ilford Orthochromatic Film was sensitised by a 5 min immersion in 0.25% ammonia and air-drying during 3 hours in a dark-room. The 18th-century manuscript piece was brought into contact with the emulsion side of the film and film and manuscript were stacked between pieces of acid-free cardboard. Both sides were covered with glassplates and the stack was pressurised by claspes. The stack was stored in a light-tight bag during 6 days. After this, the film was developed in a developing machine (developer: Ilfo Speed 2000RT; 2 min) and fixated, washed and dried.
Preparation of samples

An iron gall ink was prepared by dissolving 0.785 g gum arabic (as a solution containing 85.5 g/l, 1.050 g iron(II) sulphate, 7 aq. (Riedel-de Haen) and 1.230 g tannin (95%, Aldrich) in distilled water to a total volume of 25 ml. The molecular ratio of iron to tannin of 5.5:1 of this ink was the same as the ratio, predominant in the 104 historical ink recipes. The ink had a pH of 2.75. A plotter pen was filled with this ink. To avoid clogging of the pen, the ink was filtered through a plug of cotton-wool. With the plotter pen and a computerguided plotter the ink was applied in screen patterns to test sheets of lignin-free softwood sulphite-bleached cellulose (SSC) paper. The paper contained no fillers or sizing. Five longitudinal screen patterns, each 35 mm wide, were plotted on the A4-size sheets. The lines of the pattern were drawn diagonally to the machine direction of the paper to prevent directional preference of the mechanical test. To determine the surface pH of the ink, each sheet was provided with 6 round ink spots, 8 mm in diameter. The test sheets were cut into halves in the cross direction. One half was kept as a reference, while the other half was treated with one of the conservation treatments described below. With an extra set of sheets both halves were treated with two different treatments. Iron gall inks usually darken during the first days after application due to the proceeding oxidation of the iron(II) ions and formation of the iron(III) tannate\(^*(1)\). To ensure complete oxidation of the iron gall ink, prior to the treatments, all sheets were aged during 3 days in an oven at 70°C and 50% R.H.

Conservation treatments

Part I. During the first part of the study the following treatments were compared:

1. 30 min immersion of the sheets in an aqueous solution of sodium phytate (2.5 mmol/l), containing about 0.14% sodium - and 0.08% calcium-magnesium phytate in a molecular ratio 3:2 (Sigma). The pH of this solution initially had a value of 10.6. Previous ageing experiments had shown that too much alkalinity caused brown discoulourations of the paper, therefore the pH value was adjusted to 7.9 by adding a few drops of an aqueous solution of hydrochloric acid (1 mol/l).

2. 30 min immersion of the sheets in an aqueous phosphate solution (15 mmol/l), containing about 0.16% disodium hydrogenphosphate, 2 aq.; 0.076% calcium bis(dihydrogenphosphate), 1 aq. and 0.017% magnesium hydroxide. The total inorganic phosphate concentration, as well as the sodium - and calcium - and magnesium concentrations of this solution were equal to the total organic phosphate concentration and the respective metal-ion concentrations of the phytate solution. The pH of the phosphate solution was adjusted to 7.9 by adding a few drops of an aqueous solution of sodium hydroxide (0.3 mol/l).

Starting from solutions with the same pH and a similar total phosphate content, it was hoped that differences in ageing characteristics of the treated samples could be subscribed to the antioxidant function of phytate, because inorganic phosphate is not expected to block the Fenton reaction. Different pH values also cause differences in ageing characteristics due to acid hydrolysis, therefore a similar pH is important when comparing the effects of the phytate treatment with any other treatment. It turned out however, that the surface pH of the phosphate- and the phytate-treated samples were not similar after ageing, therefore a new set-up of the experiment was chosen, as described below.

Part II. During the second part of the study the following treatments were compared:

3. 30 min immersion of the sheets in a 0.4% aqueous solution of magnesium bicarbonate, prepared by suspending 10.0 g basic magnesium carbonate in 2.5 l distilled water and converting this compound to magnesium bicarbonate by bubbling-through carbon dioxide until the pH had reached a value of 8.2.

4. 15 min immersion of the sheets in a 0.25% aqueous solution of sodium phytate. The pH of this solution had been adjusted to 7.9 by bubbling-through carbon dioxide. To ensure similarity of pH, this treatment was immediately followed by a 30 min immersion in the aqueous solution of magnesium bicarbonate, described above.

Accelerated ageing

Part I. Reference test sheets and sheets treated with the treatments (1) and (2) were aged at 90°C and a constant R.H. of 50% in an ageing oven (Heraeus VTRK 150). The loose sheets were hanged on a grid, permitting free air-flow around them. Ageing periods of 3, 6, 9, 12 and 15 days were chosen.

Part II. Reference test sheets and sheets treated with the treatments (3) and (4) were aged at 90°C and a cycling R.H. in a programmable ageing oven (Heraeus HC0020) The ageing started at 80% R.H. After 3 hours the R.H. was decreased within 12 min to 35%. After 3 hours of dry ageing at 35% the R.H. was increased within 12 min to 80% and after another 3 hours the whole cycle was repeated. The cycle was repeated as many times as needed to reach a total ageing period of 3, 6, 9, 12, 15 or 18 days. A cycling R.H was chosen because this might cause the diffusion of iron(II) ions out of the ink regions, which would appear as the bleeding of the ink, typical of ink corrosion. The loose sheets again were hanged on a grid, permitting the air to flow freely around them.

Mechanical testing

Prior to testing, all sheets were conditioned at 23°C and a constant R.H. of 50% during at least 24 hours, according to NEN 1108\(^*(27)\). To take account of the hysteresis effect of the moisture content, before conditioning them, the unaged sheets were dried at 40°C and 25% R.H. during 2 hours.

The bursting strength of the sheets was determined according to NEN 1765 with a bursting tester (Adamel-Lhomargy CN.05) at 10 different places at the screen patterns\(^*(28)\). In this way, for each combination of ageing
period and treatment, 20 values of the bursting index were obtained. From these values the average bursting index was calculated, together with its 95% confidence region and plotted in a graph against the ageing period. The graph data were fitted according to the least-squares method, using the exponential function given below and taking account of the confidence regions (when possible these are shown in Figures 4 and 7 by vertical bars).

\begin{equation}
\text{burst index} = A \times e^{(-B \times \text{ageing period})}
\end{equation}

**RESULTS AND DISCUSSION**

**Russell test**

Figure 1 shows the Russell image obtained after 6 days of contact exposure of an ammonia-sensitised film to a piece of an 18th-century manuscript, severely damaged by ink corrosion. The image is formed by the hydrogen peroxide evolving from the ink, which proofs that increased oxidation is taking place at the ink surface relative to the surroundings. Besides the iron(II)-catalysed oxidation of cellulose, hydrogen peroxide could also be produced by the thermal oxidation of tannin. Attempts to use the Russell test to compare the results of the conservation treatments (3) and (4), described above, were unsuccessful. Another explanation for the small differences in densities of the Russell images, observed between treated and reference samples could be that the hydrogen-peroxide production by the ink is not decreased by the treatment with phytate, as it only blocks the formation of hydroxyl radicals from hydrogen peroxide, thereby inhibiting the oxidation of cellulose, but not its formation.

**Visual examination of treated samples**

The black colour of the iron gall ink on the samples treated with sodium phytate had not changed. Even after 1 month's exposure to a 0.25% aqueous solution of sodium phytate no colour changes were observed, but for a slight lightening. A brown ink was simulated by plotting an aqueous solution of iron(II)-ammonium sulphate onto a sheet of paper. The "ink" turned brown upon oxidation. This ink neither changed colour upon exposure to a neutral solution of sodium phytate. Upon exposure to an acid solution (pH = 2) however, the brown ink turned white, due to conversion of the iron(III) hydroxides to iron(III) phytate.

During the phytate treatment of the magnesium bicarbonate-treated samples (4), there formed a slight white precipitate, which was identified as magnesium phytate. As this compound is only slightly soluble in water, its formation within the paper fibres could provide an alkaline reserve against future acid contamination.

**Mechanical testing of artificially aged samples**

Part I. The unaged samples burst randomly. After 3 days of ageing at constant R.H. all untreated samples burst along the ink lines, indicating ink corrosion. With both the phosphate- and the phytate-treated samples aged at constant R.H. random bursting occurred, irrespective of the ageing period.

**Figure 4:** Bursting index (P) of reference samples (Ref.), phosphate- (Phos.) and phytate- (Phyt.) treated samples aged at 50°C and 50% R.H.

Figure 4 shows the results of the bursting test. The bursting index of the reference samples had halved within 7.0 ± 1.4 days. Both the phosphate and the phytate treatment had increased the halve-value period of the bursting index to respectively 60 ± 20 days and 40 ± 6 days. From this test, one could conclude that phosphate is a better conservation agent than phytate for treating ink corrosion. Surface-pH values of the phosphate-treated samples were higher than those of the phytate-treated samples over the whole ageing period, as shown by Figure 5.

**Figure 5:** pH-Effects on ink and paper of the phosphate- (Phos.) and the phytate treatment (Phyt.) upon ageing at 90°C and 50% R.H.; Ref. = reference

This difference could explain the lower degradation rate of the phosphate-treated samples, as both the acid hydrolysis and the oxidation are slowed down at higher pH values, as long as these are lower than pH = 9.1.
Phosphate is not expected to cause any inhibition of the oxidation by complexation of iron(II) ions. A good comparison therefore can only be made when both treatments have caused the same pH on the paper and the ink. For this reason the treatments (3) and (4) were chosen to compare.

Part II. The unaged samples burst randomly. After 3 days of ageing at a cycling R.H. all untreated samples showed bursting along the ink lines. Until 12 days of ageing, the treated samples showed random bursting and there was no difference in bursting behaviour between the differently treated samples. At longer ageing periods however, differences in bursting behaviour between the samples treated with treatment (3) and (4) began to show up. The samples treated solely with magnesium bicarbonate (treatment (3)) began to burst at the ink lines, while those treated with phytate and magnesium bicarbonate (treatment (4)) continued to burst randomly, as is shown in Figure 6 for treated samples, aged 15 days.

At 18 days of ageing the samples treated with phytate and magnesium bicarbonate showed more bursting along the ink lines than at 15 days. Therefore, even the combined treatment did not completely stop ink corrosion.

The different bursting behaviour of the treated samples at ageing periods, longer than 9 days correlated with different bursting indexes, as can be seen in Figure 7. The samples treated with magnesium bicarbonate had lower bursting indexes than those treated with the combined treatment. The half-value period of the bursting index of the samples treated with (3) was 15 ± 1 days, while that of the samples treated with (4) was 23 ± 1 days. Both treatments had increased the stability of the paper samples; the half-value period of the bursting index of the untreated samples was 5.6 ± 1.0 days. The surface-pH values of the samples treated with the combined treatment were similar to those of the samples treated with magnesium bicarbonate, as can be seen in Figure 8. Therefore, the slower mechanical deterioration of the samples treated with phytate and magnesium bicarbonate must be due to the anti-oxidant function of phytate.

Another effect of the treatments can be seen from the fact that both ageing curves show two distinct parts.

Until 9 days the bursting index of the treated samples decreased little. After this period it decreased faster for both treatments, the samples treated with magnesium bicarbonate lost their strength faster than their counterparts. A closer inspection of the ageing curve of the reference samples shows us that the points at 3 and 6 days deviate from a true exponential curve. This deviation is caused by cross-linking, a radical process leading to a temporary increase of the wet strength of the paper. Both treatments have slowed down this process, causing the maximum deviation to shift from 3 days for the reference samples to 9 days for the treated ones. To obtain a good comparison between conservation treatments with an accelerated ageing test, the ageing period always should be chosen within the second part of the curve, where chain scission is more important than cross-linking.

The half-value period of the bursting index for ageing at a cycling R.H. (5.6 ± 1.0 days) is considerably lower than the half-value period obtained with the untreated samples aged at a constant R.H. (7.0 ± 1.4 days). This indicates that the changing R.H. accelerates the degradation of paper, possibly by increasing the oxidation rate. The change from a dry to a moist ageing causes the formation of radicals, as was shown by the chemiluminescence technique. The paper also showed more yellowing, especially when comparing the treated samples. Aqueous treatments change the accessibility of the paper, thereby increasing the speed of dehydration during drying. The presence of alkaline substances can lead to the formation of brown products at high pH values through a combination of alkaline hydrolysis, dehydration and oxidation. With the treated and aged samples, wetting by a drop of water caused migration of brown products, producing a brown edge at the dry interface. Drying at metal grids of the sheets treated with sodium phytate had caused accumulation of this compound at the contact places and the edges of the paper due to the migration of sodium phytate. During accelerated ageing brown stains had formed at these places, possibly due to a higher alkalinity. Changing from sodium- to the less-soluble magnesium phytate could prevent this, because the latter compound will not migrate.
CONCLUSIONS AND FUTURE RESEARCH

Catalysis of cellulose oxidation takes place by the excess iron(II) ions present in most iron gall inks and is the second cause of ink corrosion after acid hydrolysis. A changing relative humidity accelerates ink corrosion. It also speeds up the diffusion of iron(II) ions out of the ink regions, causing the formation of brown ink bleedings, characteristic of ink corrosion. Paper artefacts which are threatened by ink corrosion therefore must be stored at a constant R.H. The bursting test on artificially aged iron gall-ink patterns provides an accurate means to evaluate the effects of conservation treatments on ink corrosion. During the first ageing period cross-linking can prevail over scission reactions, resulting in a very slow deterioration rate, which is similar for different treatments. After this period, scission reactions dominate, resulting in higher deterioration rates, which differ for different treatments. Therefore, in order to evaluate the effects of conservation treatments, ageing periods should be chosen long enough to reach the latter period. According to the results of these tests, the treatment with an aqueous solution of sodium phytate leads to a remarkable protection of paper samples against ink corrosion. Its protective function can be explained by the blocking of the formation of hydroxyl radicals from hydrogen peroxide after complexation of iron(II) ions. Because of this, the iron(II) catalysed oxidation is slowed down.

Additionally, a phytate treatment could also be used to deacidify the paper. Sodium phytate might cause the formation of brown stains at places of accumulation, due to a high pH. This could be prevented by changing to the less-soluble magnesium phytate. This compound could also provide an alkaline reserve against future acid formation in the paper. Research is started to test the effects of a treatment with an aqueous solution of magnesium phytate and ammonia (pH = 7.8) on ink corrosion, using the accelerated ageing at a cycling R.H., described above. I hope to present some results of these new tests at the IADA conference in Tubingen, September 1995.

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SUMMARY

Ink corrosion, the degradation of paper artefacts by iron gall inks is caused by acid hydrolysis and iron(II)-

Figure 8. pH-Effects on ink and paper of the treatments upon ageing at 90°C and 80/35% R.H.; Ref.: reference, Ph: phytate-treated, M: magn. bicarb.-treated
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REFERENCES


[14] Barrow, W.J.: Manuscripts and Documents, Their Deterioration and Restoration. Charlottesville: University of Virginia Press, 1955, Table 1


15 Exponential function used: \[ P = A \, e^{-B \, t} + C; \] 
\[ P = \text{bursting index}, \, t = \text{ageing period}; \, A, B \, \text{and} \, C \, \text{are constants} \]