

Ink corrosion: comparison of currently used aqueous treatments for paper objects

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Abstract

The controversial topic regarding active treatment of ink-corroded artefacts still causes concern in the field of paper conservation. Especially, the effectiveness of treatments and their long-term side effects are often a cause to anxiety. Based on the results of a literature survey, it was thought necessary to compare nine commonly used aqueous treatments in an attempt to understand the processes involved better and answer some of the previously unsolved questions. Their efficacy in delaying ink corrosion, as well as immediate and long-term side effects accompanying the treatments, was investigated.

Standard reference papers (cotton linters) with an applied "corrosive" iron gall ink and four original, iron gall ink written artefacts (17th and 19th century) were immersed twice for 20 minutes in fresh treatment solutions. The efficacy to delay the degradation process was determined by measuring the pressure required to burst artificially aged (90°C, 35/80% RH) standard reference papers (bursting strength). Side effects such as mechanical decay, colour changes of papers and inks, "bleeding" of inks, crystal formation and changes in ink texture were determined after treatment by visual examination. Measurements of the yellowness index were used to indicate colour changes of the paper after treatment and after artificial ageing.

Best results, which include an effective delay of ink corrosion as well as minor side effects, were achieved by immersing treating papers with a combined calcium phytate / calcium bicarbonate treatment as well as a single calcium bicarbonate treatment.

Zusammenfassung

Noch immer ruft die kontrovers diskutierte Frage der Behandlung tintenfraßgeschädigter Papiere Besorgnis unter den Papierrestauratoren hervor. Vor allem die Effektivität der gegenwärtig verwendeten Methoden sowie deren zu erwartenden Nebenwirkungen geben Anlaß zu einer deutlichen Verunsicherung. Basierend auf einer Auswertung der relevanten Tintenfraß-Literatur erschien es notwendig, die neun gegenwärtig am häufigsten verwendeten wässrigen Behandlungsmethoden miteinander zu vergleichen. Kriterien der Beurteilung waren einerseits die Effektivität der Methoden den Tintenfraßprozeß zu stoppen, sowie andererseits deren Nebenwirkungen direkt nach der Behandlung und nach künstlicher Alterung.

Standard-Referenzpapiere (cotton linters) mit einer darauf applizierten „korrosiven“ Eisengalltinte und vier mit Eisen-

galltinten beschriebene Originale (17. und 19. Jh) wurden je Behandlungsmethode zweimal für 20 Minuten in ein Bad gegeben. Wie effektiv die Behandlungen den Tintenfraß zu stoppen in der Lage waren, wurde mit Hilfe von Berstdruckmessungen (NEN 1765) an den gestaffelt künstlich gealterten (90°C, 35/80% RH) Standard-Referenzpapieren ermittelt. Nebeneffekte wie mechanische Schäden durch die wässrige Behandlung, Farbveränderungen von Tinten und Papieren, das „Ausbluten“ der Tinten, Kristallbildung auf der Oberfläche und Veränderungen der Tintentextur wurden an den Originalen visuell beurteilt. Auftretende Veränderungen der Papierfarbe infolge der Behandlung sowie nach der künstlichen Alterung wurden mit Hilfe colorimetrischer Methoden ermittelt (Reflected Light Spectrophotometer: Minolta CM 2002).

Die geringsten Nebenwirkungen, sowie einen effektiven Schutz gegen Tintenfraß erzielte die kombinierte Behandlung mit Kalziumphytat / Kalziumbikarbonat, gefolgt von einer Behandlung mit Kalziumbikarbonat.

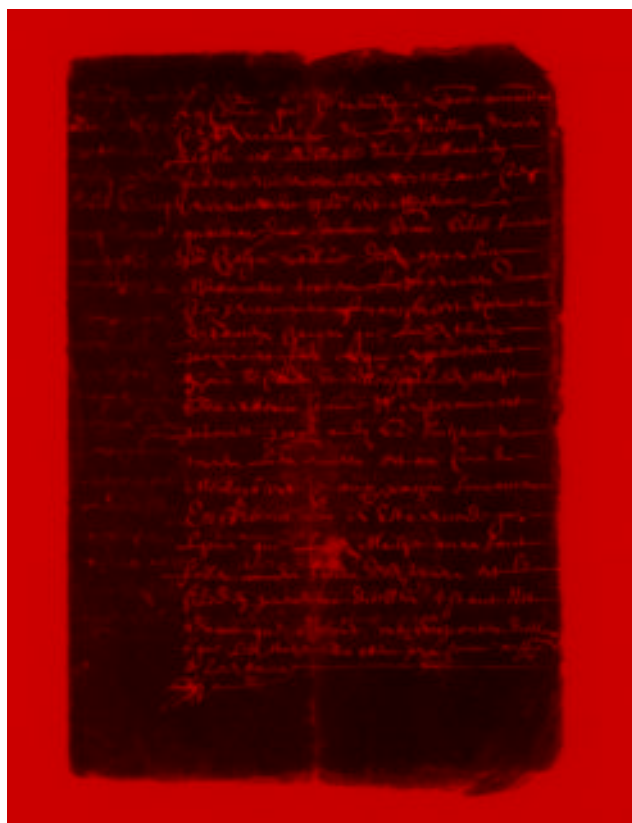


Fig. 1 Ink-corroded artefact, France, 1620

1. Introduction

The active conservation of iron gall ink-corroded paper artefacts is still a field of controversial discussion. Whereas some conservators hesitate to treat at all, others tend to choose non-aqueous treatments. The use of aqueous treatments is usually accompanied by scepticism as there are questions regarding their long-term effect. An aqueous treatment for ink-corroded artefacts presents some serious risks, but – and this should not be underestimated – it provides all the benefits usually produced by aqueous treatments.

Prior to this investigation, a literature survey has been carried out in order to get an overview of internationally used aqueous methods to treat ink corrosion. On the basis of the practical experiences published by paper conservators, risks and benefits of commonly used aqueous treatments were outlined (Reißland 1999). The survey indi-

2. Experimental

To determine the efficiency of the tested methods to delay ink corrosion, a standardised procedure had to be chosen. Such a procedure was developed by Neevel, determining the bursting strength according to ISO 2758: 1983 (NEN 1765) on standard reference test papers. Because this does not provide sufficient information concerning side effects occurring on original artefacts, it was necessary to treat originals as well.

2.1 Sample preparation

- Iron gall ink
- To prepare "corrosive" ink, showing a typical excess of iron

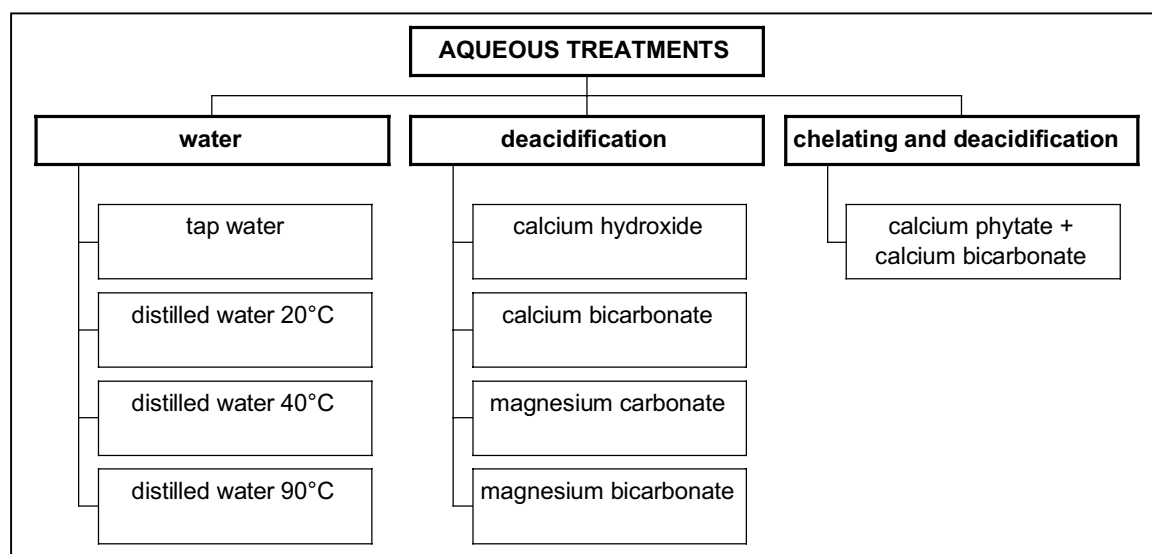


Figure 2. Overview of tested aqueous treatment methods

cated that some research already has focused on the comparison of aqueous treatments, among them investigations carried out by Brannah 1975, Hey 1981, Lienardy and van Damme 1991, Porck and Castelijns 1991, Heller et al. 1993 and Neevel 1995.

One conclusion drawn from the literature survey was that several aqueous treatments are in use around the world. Some featured constantly over the years, for example the calcium bicarbonate treatment, whereas others, for example the "boiling method", re-occurred occasionally.

In this article, a comparison of nine aqueous treatments for iron gall ink corrosion is presented (see fig.2). Besides eight generally used treatments, a calcium phytate treatment in combination with a calcium bicarbonate treatment was additionally included, because it achieved very good results during its testing period (Neevel and Reißland, 1997).

For the paper conservator, two points are of main importance – firstly, that the delay to the ink corrosion process maximised and secondly, that side effects (like colour changes of inks or "bleeding") are as insignificant as possible. Therefore the following issues were chosen as criteria for comparison of the nine treatments:

- their efficiency to delay ink corrosion
- their immediate side effects
- their long-term side effects

sulphate, a molar ratio Fe : Tan of 5.5 : 1 was chosen. The ink was prepared by dissolving 3.14 g of gum arabic, 4.2 g iron(II) hepta sulphate (Riedel de Haën) and 4.92 g of tannin (95%, Aldrich) in 0.1 l of distilled water. The pH of the ink reached a value of 2.8.

- Standard reference papers

A non-sized, cotton-linters cellulose paper bleached with elemental chlorine and hypochloride, in DIN A4 size was used. It contained no fillers. To apply the ink, a computer plotter (Hewlett Packard 7475A) was used, fitted with a 0.5 mm pen. Five longitudinal screen patterns (about 35 mm wide) were plotted. To prevent directional preference, the screen patterns were applied diagonally to the grain direction of the paper. Each A4-sheet was additionally provided with 8 round ink spots, 8 mm in diameter for surface-pH measurements. To avoid clogging of the plotter pen, the ink solution was filtered through a plug of cotton wool when filling the pen.

The papers were pre-aged for 3 days in an oven at 70°C and 50% relative humidity (RH) and then cut into 2 halves, each of A5 size. All 10 treatment sets consisted of 8 sheets each.

- Originals

Paper: Four original artefacts were chosen for the investigation, see table 1. The 17th century papers were hand made

date	place	fibre analysis	paper making	watermark
23.10.1620	France	cotton + linnen (rag)	hand made	-
22.4.1683	France	cotton + linnen (rag)	hand made	-
23.6.1896	The Netherlands	cotton + linnen	machine made	+
24.7.1898	The Netherlands	cotton + linnen	machine made	-

Table 1. Originals - date, origin and fibre analysis

date	ink colour	signs of ink corrosion	Fe(II)-test Ink
23.10.1620	dark brown	mechanical damage	pos.
22.4.1683	dark brown	-	pos.
23.6.1896	brown	fluorescence verso	pos.
24.7.1898	dark brown	fluorescence verso	pos.

Table 2. Originals - characteristic ink properties; signs of ink corrosion

rag papers, the 19th century papers machine made papers. The paper from 1896 has a watermark (Old Berkshire Mills 1895) and a machine made sieve structure. Every original artefact was cut in 10 pieces, one for every treatment.

Inks: Because no specific test for iron gall inks currently exists, it is difficult to distinguish the writing fluids used. Measurements, using the non-bleeding iron(II) test developed by Neevel (bathophenanthroline in ethanol)[1] indicated iron ions in all inks. Unfortunately it has to be pointed out that a positive iron test does not allow a distinct identification of iron gall inks, because other inks can be contaminated with iron.

One can assume that the two 17th century inks belong to the group of iron gall inks, because no other writing liquid was in common use during the 17th century. It was more difficult to determine whether or not two 19th century inks are iron gall inks. Several blue or black coloured inks (like the chrome logwood inks or the black aniline inks) came on the market during the second half of the 19th century. Further examination was necessary. The verso-sides of both documents showed a very slight browning in daylight as well as some fluorescence (at 365 nm) under the inked areas. According to previous tests, this is the first sign of deterioration of the paper support in the case of iron gall ink corrosion (Reißland: 1999). The positive iron test and the paper's fluorescence reinforced the assumption that the documents were written with iron gall inks.

Ink corrosion: Only the original dating from 1620 was mechanically damaged in the ink areas. The other artefacts showed only very early stages of corrosion (fluorescence under the ink lines).

2.2 Treatment solutions

- Distilled water (at 20°C, 40°C and 90°C).

Before treatment, the temperature of the water was adjusted at 20°C in a water bath. The higher temperatures (40°C and 90°C) were achieved by using a heating plate and stainless steel trays. If the water reached temperatures above 80°C strong water movement (formation of air bubbles) occurred.

- Tap water (Amsterdam Rivierduinwater)

The content of transition metals, which might catalyse the oxidative degradation process like iron (0,01 mg/l), copper (0,028 mg/l) and manganese was quite low, as was

the total chlorine content (not detectable). A positive influence can be expected from the high calcium and magnesium salt content (German Degree of Hardness of 8.6 (D)). For the specified data see [2].

- Calcium hydroxide

2 g of powdered calcium hydroxide was dissolved in 1l of distilled water stirred thoroughly and allowed to settle for one night. This saturated solution had a pH value > 12. Before use the solution was decanted, so that no precipitate was left. Then the solution was diluted with distilled water until a pH-value of approximately 10 was achieved.

- Calcium bicarbonate (saturated)

1,1 g of calcium carbonate was dissolved in 1l of distilled water and carbon dioxide was continuously passed through for 3 hours and stirred thoroughly. Some white powder remained at the bottom of the bottle.

- Magnesium carbonate (saturated)

0,93 g of magnesium carbonate was dispersed in 1l of distilled water and stirred thoroughly. White powder remained at the bottom of the bottle.

- Magnesium bicarbonate (saturated)

18,3 g of magnesium carbonate was dissolved in 1l of distilled water and carbon dioxide was continuously passed through for 3 hours. White powder remained at the bottom of the bottle.

- Calcium phytate

0,44g of calcium carbonate was slowly added to 2,28g of phytic acid (50.4% solution, Mitsui Chemicals). Formation of bubbles (CO₂- evolution) was observed during the reaction. 1l of distilled water was carefully added by continually stirring the solution. Due to addition of some ammonium hydroxide (25% in weight) the pH increased and reached a value of 5,8. Due to the increase in pH the previously clear solution turned milky-white.

2.3 Treatment procedure

Test papers and original papers were treated separately; thus the solutions were also individually prepared. To ensure a standardised washing procedure for both methods, equal treatment steps were undertaken.

The dry papers were immersed in the treatment solution for 20 minutes. Because of the different amounts of paper, the standard reference papers were treated with 2l of solution, whereas the

treatment		pH		temperature (in °C)	
		cotton-linters	originals	cotton-linters	originals
1	no treatment (reference)	-	-	-	-
2	dist. water 20°C	5.85	5.3	20	20
3	dist. water 40°C	5.6	5.85	40	40
4	dist. water 90°C	5.6	6.3	~ 90	~ 90
5	tap water	7.65	7.85	17.5	14
6	calcium hydroxide	10.2	10.15	22.5	22
7	calcium bicarbonate	5.8	5.9	16.5	14
8	magnesium carbonate	10.5	9.4	19	21
9	magnesium bicarbonate	7.0	7.2	23	22
10	ca-phytate + ca- bicarbonate	5.8	5.8	22	28
		5.8	6.2	22	23

Table 3. Mean pH and temperature values of the treatment solutions; grey highlighted fields indicate an alkaline pH-level

originals required only 1l due to the smaller amounts. A second bath followed, which contained the same amount of fresh solution; again papers were immersed for 20 minutes. The mean temperature and pH-values are listed in table 3. The wet objects were then allowed to dry between felts without pressure.

2.4 Artificial ageing

In order to follow the progress of ink corrosion, the standard reference papers were artificially aged. Every treatment set consisted of 8 sheets of paper. While 2 papers of each set remained unaged, 2 papers were aged for 6 days, 2 papers for 12 days and 2 papers for 18 days in a programmable oven (Heraeus HC0020) at 90°C with a relative humidity (RH) cycle, every 3 hours, between 80% and 35%. The papers were suspended individually on a grid in the oven, permitting free airflow around them.

The originals were cut into 2 pieces, one piece remained unaged, the other piece was aged under the same conditions as the standard reference papers (i.e. 90°C and changing relative humidity of 35%-80%), but for 15 days. After that period they showed distinct signs of ink corrosion.

2.5 Testing methods

- Bursting strength

The pressure required to burst a paper indicates its mechanical (bursting) strength. In the case of ink corrosion, the degrading effect of the ink causes a decrease in paper strength. Therefore the bursting test can be used to determine if a treatment effectively enough delayed the degradation process. The bursting strength was determined using a bursting tester (Adamel - Lhomargy CN.05). The standard reference papers were conditioned for 24 hours at 23 (1°C and 50 (2% RH prior to testing (NEN 1108)). On every test paper 10 measurements were performed in different places on the screen-patterned area. In this way, 20 values were obtained due to the duplicate test papers of each set. Average values were calculated and plotted against the ageing periods.

- Yellowness index (Paper discolouration) The yellowness index is an indication of the degree to which a specimen sur-

face is different to the ideal white in the yellow direction. It is used here to indicate the influence of a treatment on the change of paper colour during ageing. A reflected light-spectrophotometer (Minolta CM 2002) was used (ASTME 313, reapproved 1987) under an observation angle of 10 (SCI Illumination 1 and 2: D65). 3x4 values on different locations were measured on each paper. In this way, 24 values were obtained due to the duplicate test papers of each set and the average was calculated.

- Visual examination

Test papers and originals were examined in day light as well as under UV using an UV lamp (365nm). Furthermore a microscope was used for the examination.

3. Results and Discussion

3.1 Treatment-efficacy to delay ink corrosion

Determination of the bursting strength presented some difficulties. Due to a high amount of ink (compared to papers from the former testing series about 2 times as much ink), the paper strength decreased so drastically, that after 6 days of artificial ageing, the bursting tester was not sensitive enough to obtain results for the untreated (strongly degraded) reference papers. After 12 days, most of the results of the artificially aged test papers were around or under the detection limit of 10 kPa. After 18 days only a few, but significant results were obtained.

After the treatments (0 days aged), the paper strength of treated and untreated papers was more or less comparable. After 6 days of artificial ageing the pressure required to burst the papers was lower in all cases. Nevertheless - in comparison to the untreated references (first column of fig. 3), all treatments delayed the loss of the mechanical strength of the papers.

To discuss the results, it is necessary to remember that two degradation processes cause ink corrosion; acid-catalysed hydrolysis and iron(II)-catalysed oxidation of cellulose. To delay ink corrosion, both degradation processes have to be stopped and further decay has to be prevented. The nine treatments can be divided in 3 groups: washing (column 2-4), deacidification (column 3-9) and a combination of chelating and deacidification (column 10).

Bursting Strength

(Serie: aqueous treatments, 2/99)

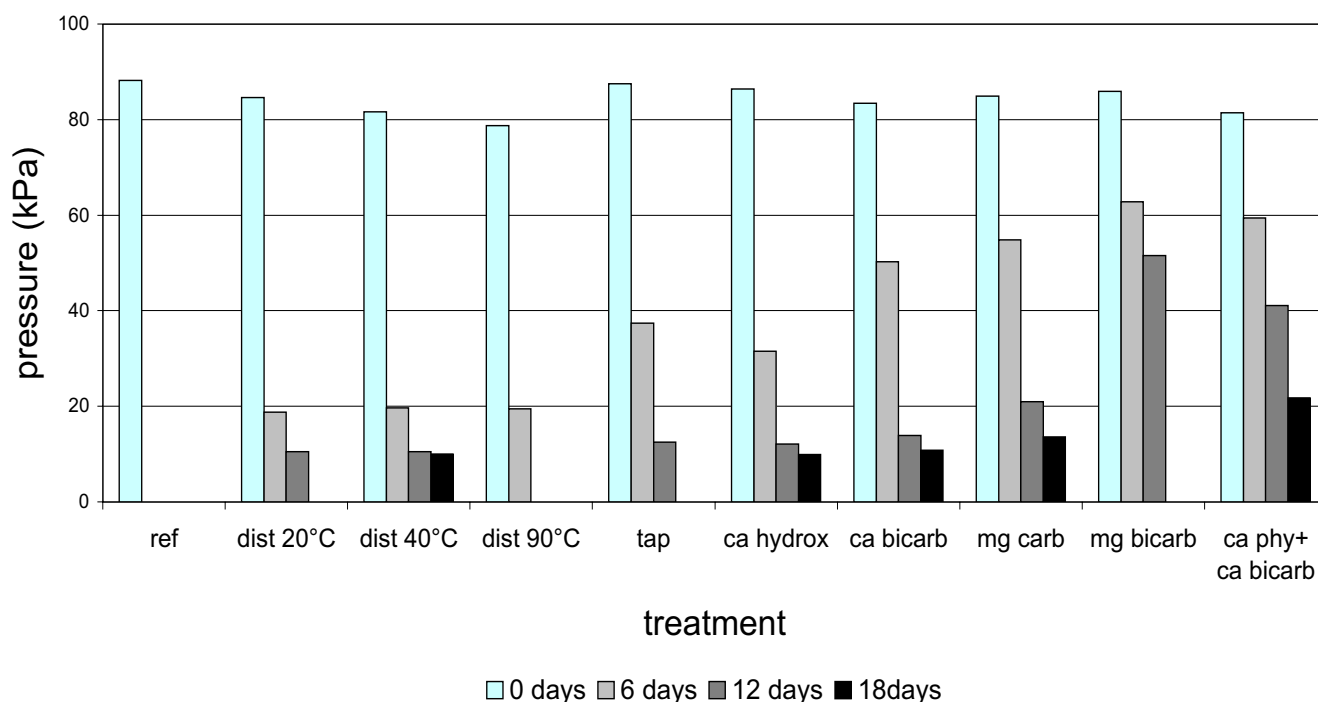


Figure 3. Bursting strength measurements of standard reference papers, treated in nine different ways and aged for 0, 6, 12 and 18 days at 90°C and 80/35% cycling RH (if no value for aged papers is indicated, the bursting strength falls below the detection limit, like e.g. for the reference papers after 6, 12 and 18 days)

• Washing

Washing delays the degradation in so far as the iron(II) ions (delay in oxidation) and acid paper-degradation compounds (delay in acid hydrolysis) are washed out. However, decay will not be prevented in the future. Therefore washing with distilled water was least effective in delaying the degradation. Increase in temperature did not influence this result.

• Deacidification

During deacidification, paper degradation compounds are washed out. Additional to that, deacidification prevents further acid hydrolysis. Furthermore, for a certain period it also prevents oxidation, because iron(II) ions are oxidised in alkaline environments to iron(III) ions, which are not able to catalyse the oxidation. However, it is just a matter of time until this process is reversed. The least effective deacidification agents were calcium hydroxide and tap water. Magnesium carbonate and calcium bicarbonate impart a comparable amount of alkaline reserve in the paper, while magnesium bicarbonate introduces ten times as much. This does not automatically mean, that this method is ten times as effective. High pH ranges achieved after drying (ca. pH 10) might be the cause of alkaline hydrolysis. This might explain the initial very good results, but rapid degradation after 12 days of artificial ageing.

• Chelating + deacidification

Calcium phytate, as chelating agent, can bind complex iron(II) and iron(III) ions without harming the ink (Neevel 1999). This means that free iron ions are chelated and therefore can not accelerate the oxidation process. Combined with a calcium bicarbonate treatment, ink corrosion is effectively delayed, because both degradation proc-

esses are stopped. Furthermore an oxidation reserve as well as an alkaline reserve are deposited in the paper, preventing further decay. This is confirmed by the bursting strength measurements, which show that the calcium phytate/calcium bicarbonate is the most effective treatment to delay ink corrosion.

Considering the total ageing period, calcium bicarbonate and magnesium carbonate achieved considerably good results. The best protection against ink corrosion was provided by the combined treatment using calcium phytate followed by a calcium bicarbonate treatment.

3.2 Immediate side effects

Treatment of ink-corroded papers can cause side effects, which become visible during or after the treatment or after the drying:

- mechanical damage
- change in paper appearance
- colour change of ink
- dissolving of ink compounds (“bleeding”)
- crystal forming
- changes in the texture of the ink surface

Side effects of treatments can only be determined, if aged inks are treated. Therefore, four naturally aged originals were treated and examined in daylight, under the microscope and using an UV-lamp (365nm).

• Mechanical damage

Aqueous treatments can cause mechanical damage on objects, showing further stages of degradation. Previous investigation (Reiß-

land 1999) showed that the water penetration behaviour of the inked paper areas changes with respect to their stage of degradation. At the early stages (fluorescence or light brown discolouration) the areas surrounding the ink are hydrophilic, they easily absorb water. Areas showing a further degree of decay (dark brown discoloured) behave hydrophobically and water hardly penetrates these areas. If ink-corroded papers are wetted with water, tensions are created between the hydrophilic and the hydrophobic areas. The degraded paper can not withstand that tension and breaks - mechanical damage occurs in the inked areas.

The treated originals in this investigation did not show a distinct decay, with exception of the paper dated from 1620. This was discoloured to a dark brown colour on the backside under the inked areas and showed signs of mechanical decay. After all aqueous treatments, mechanical damage increased only on the degraded paper, especially in the dark brown discoloured areas. Pre-wetting using ethanol or iso-propanol (or a mixture of water and an alcohol) can prevent this mechanical damage, because the hydrophobic areas are easily penetrated by alcohol (Reiðland 1999).

- Change in paper appearance

During the washing of papers, paper degradation products, which are often coloured, are dissolved causing a whiter appearance of papers after washing. Whitening of the paper alters the contrast between the dark ink and the paper tone. This should be considered when treating drawings. The solubilities of the compounds are mainly dependent on three factors. Firstly, dissolution of the salts in the paper can be decreased due to the presence of ions or salts in the washing solution (like in the case of tap water or deacidification solutions). Distilled water however, tends to dissolve every water-soluble compound quite aggressively (see also Tang et al. 1979). Secondly, the pH-effect has to be considered. Alkaline solutions dissolve acid paper degradation products easier than solutions at an acid or neutral pH. Finally, increased temperature usually increases the solubility of compounds, except for calcium and magnesium carbonates. Table 4 shows the results that were achieved by yellowness index measurements of the treated papers, as confirmed by visual examination.

In general, all treated papers show a whiter appearance than the untreated reference papers. Papers treated with magnesium carbonate and magnesium bicarbonate appear, in most cases, whiter than all the other treated papers. One cause of this whiter appearance might be the white deposit of crystals on the sur-

paper appears whiter					
	treatment	1620	1683	1896	1898
1	no treatment (reference)				
2	dist. water 20°C	+	+	++	+
3	dist. water 40°C	++		++	+
4	dist. water 90°C	+	+	+	++
5	tap water	++		+	
6	calcium hydroxide	++		++	+
7	calcium bicarbonate	+		++	+
8	magnesium carbonate	+++	+	++	++
9	magnesium bicarbonate	++	++	+++	++
10	ca-phytate + ca-bicarbonate	+++	+	+	

Table 4. Paper appearance after treatment compared to the untreated reference: + minimal whiter ++ whiter +++ clearly whiter

faces of the ink and paper, especially for the samples treated with magnesium bicarbonate. Furthermore, the alkaline pH of the magnesium carbonate solution might have caused an increased solubility of acid degradation products.

Washing in distilled water (20°C, 40°C and 90°C), calcium hydroxide and calcium phytate / calcium bicarbonate resulted in comparable whitening of the papers. This result did not meet the theoretical expectations, that boiling (high temperature) and calcium hydroxide (alkaline pH) treatment cause increased whiteness [3].

After treatments with tap water and calcium bicarbonate, the paper colour changed less.

- Colour change of ink

Freshly produced iron gall ink usually has a bluish black tone. But interestingly, most of the naturally aged inks today appear brown, varying from dark brown to a faint yellowish colour. Reasons for this colour change are not yet fully understood. In order to explain this behaviour, Krekel (1999) developed a theoretical model, which states that the ink complex is irreversibly destroyed by acid catalysed reactions, which occur during natural ageing, as well as under alkaline conditions in pH ranges above 7.5. The remaining reaction products are brown coloured. Consequently, also treatment in acid or alkaline pH-ranges might destroy the ink complex, causing a change in ink colour to a brown tone.

A second factor to consider is the removal of coloured, water-soluble ink compounds, or ink degradation products, as a result of washing. This might cause a lighter ink appearance after treatment. The treated samples were examined under the microscope and in daylight. Difficulties in interpretation arose as the contrast between papers and inks increased visibly and because white crystals were deposited on the surfaces of inks. Table 5 summarises the results.

colour change of ink					
	treatment	1620	1683	1896	1898
1	no treatment (reference)				
2	dist. water 20°C	++		++	
3	dist. water 40°C	++		++	
4	dist. water 90°C	++		++	++
5	tap water	++			
6	calcium hydroxide	++		++	
7	calcium bicarbonate	++			
8	magnesium carbonate	++			++
9	magnesium bicarbonate	++			++
10	ca-phytate + ca-bicarbonate	+			++

Table 5. Colour change of ink + discernible ++ obvious +++ strong

Three of the four inks showed colour changes due to treatment measures. The inks from 1620 and 1899 changed to a slightly lighter brownish tone, the ink from 1896 to a blackish blue tone after washing in distilled water qualities and to brown after calcium hydroxide treatment.

The use of water at a temperature of 90°C noticeably changed ink colour, which may be attributed to its good dissolving properties as well as the continued movement during the treatment due to the boiling of water. Calcium hydroxide, magnesium carbonate and magnesium bicarbonate caused a distinct change in ink colour. Minor changes in ink colour were obtained by using tap water and calcium bicarbonate.

- Dissolving of ink compounds (“bleeding”)

Ink compounds can be dissolved and diffuse into the surrounding solution (clouds of discoloured matter above the ink), but might also migrate inside the paper causing the discolouration of areas around the ink. Usually the term “bleeding” is used to describe this phenomenon. Some water-soluble ink compounds are visible like dyes or tannin-degradation products; others are invisible like iron(II)-ions. Some become visible under UV.

Preliminary tests were carried out concerning the determination of iron ions in treatment solutions after treatment. In general it can be stated, that treating samples in distilled water causes a significant removal of iron(II) ions (10-15 %). The low iron(II) ion content measured in the alkaline solutions (1-2%) might be due the oxidation of iron(II) to iron(III), which is favoured at higher pH. Further research will focus on the spreading behaviour of iron ions as a result of aqueous treatments.

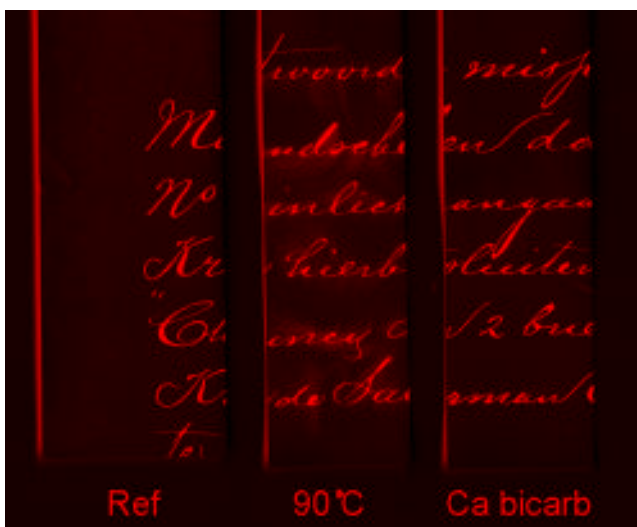


Figure 4 Sample from 1896: Dissolving of ink compounds is clearly visible after the treatment with distilled water (90°C), while a calcium bicarbonate treatment did not cause any “bleeding”

“Bleeding” was detected on the originals dating from 1620 and 1896. Distilled water caused the most pronounced “bleeding” of these inks due to its efficient property of dissolving water-soluble compounds. Calcium hydroxide dissolved brown coloured ink products. Its alkaline pH could not be the reason for the dissolution. If this were the case, then the magnesium carbonate solution would also have shown similar results. Perhaps, the increased bleeding is due to the fact that the calcium hydroxide solution was not saturated, but was fully dissolved in distilled water achieving a pH-value of 10.2.

- Crystal deposits

Crystal deposits can be found on the surface of original inks, but can also be formed as a result of treatments. Furthermore, saturated solutions with a visible precipitate can deposit crystals on the surface of the object.

Before treatment, no crystal formation could be observed on all ink surfaces. After treatment, all deacidification treatments caused white deposits on the ink surfaces, see table 6.

White deposits were noticed even by the eye, for the magnesium bicarbonate treated papers. In this case, the precipitate of the solution probably deposited on the object’s surface.

paper appears whiter					
treatment		1620	1683	1896	1898
1	no treatment (reference)				
2	dist. water 20°C				
3	dist. water 40°C				
4	dist. water 90°C				
5	tap water				
6	calcium hydroxide				+
7	calcium bicarbonate	+		+	+
8	magnesium carbonate	++			+
9	magnesium bicarbonate	++	+++	+++	++
10	ca-phytate + ca- bicarbonate	++	++	++	++

Table 6. White, crystalline deposits on ink surfaces: + some few crystals, ++ ink covered with crystals, +++ thick deposit

White crystals might have been formed as a result of deacidification treatment. The reaction of sulphuric acid [4] with calcium- or magnesium ions forms white salts (magnesium- or calcium sulphates) which are only partially soluble in water. Because sulphuric acid is situated mainly in- and around the inks, the salts will precipitate in these areas. This was confirmed by examination of the treated objects. White, powdery deposits were observed on all of the ink surfaces after deacidification treatments. Treatment with calcium phytate could also cause the formation of white iron phytate.

- Changes in the texture of the ink surface

Changes in the ink texture after aqueous treatments were difficult to ascertain even with microscopical examination. White crystalline deposits complicated the evaluation. Most apparent was the negative influence of the washing with hot distilled water. Ink particles were removed and the inks appeared more dull and “washed out”. This is in contrary to the findings of Biggs (1998), who achieved beneficial results using distilled water at 90°C.

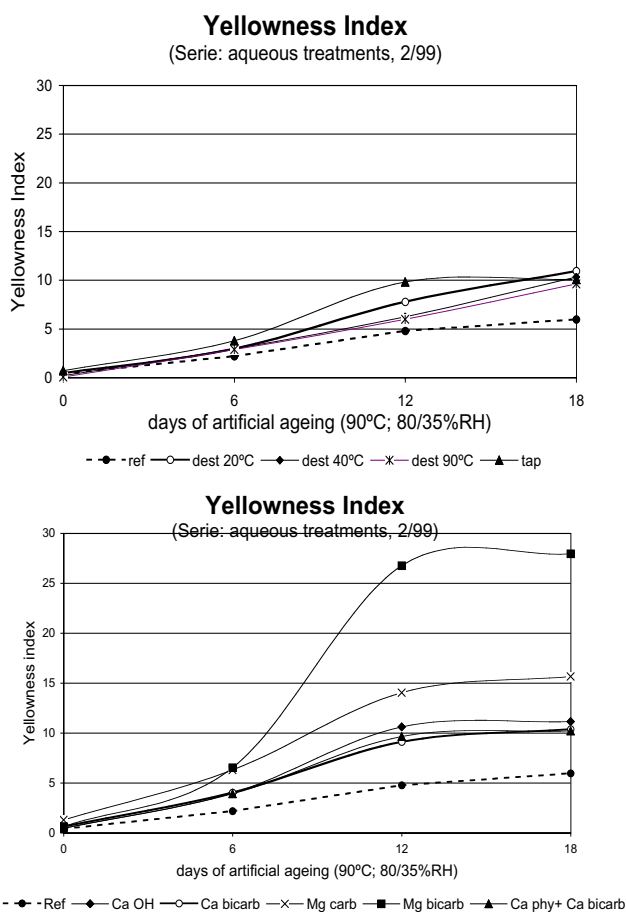
3.3 Long term side effects

Long-term side effects of treatments can be determined by examination of artefacts that were treated in the past or that were artificially aged. In this investigation, treated test papers and treated originals were artificially aged. Obvious was a colour change in the paper as well as the ink. In order to follow the change in paper colour, the yellowness index was measured on the tested standard reference papers, see figures 5 and 6.

In comparison to the reference, all treatments caused an increased yellowing after artificial ageing. The degree of yellowing is quite similar for most of the treatments except those using magnesium salts for deacidification. While magnesium carbonate treatment caused an increased browning, papers treated with magnesium bicarbonate were discoloured to a yellowish tone. This discolouration is quite irregularly distributed over the paper, which complicated the measurements. The high pH-values achieved after drying of the papers (ca. pH 10.2) might be the cause of this colour change.

Conclusions

The protective effect of a treatment against ink decay is indicated by the bursting strength measurements. Best results in delaying ink



Figures 5 and 6. Yellowness index of treated standard reference papers, aged for 0, 6, 12 and 18 days at 90°C and 80/35 % cycling RH

corrosion were achieved with the calcium phytate/calcium bicarbonate treatment, which provides the possibilities to delay both degradation processes.

Good protection against ink corrosion was provided by all deacidification treatments, despite tap water and calcium hydroxide, which might have not introduced sufficient alkaline reserve to the papers. Magnesium bicarbonate treated standard reference papers interestingly showed rapid degradation after an artificial ageing period of 18 days (90°C, 35/80% RH).

Least effective in delaying ink corrosion were the washing procedures using distilled water, even if the water temperature was adjusted at 90°C.

Ink colour changes and “bleeding” of the inks increased due to treatments with distilled water qualities and calcium hydroxide. Least changes occurred using tap water, calcium bicarbonate and calcium phytate/calcium bicarbonate. Crystal formation on the ink surfaces occurred after all deacidification treatments, but is most pronounced after a magnesium bicarbonate and a calcium phytate/calcium bicarbonate treatment. Because the presence of a precipitate in a solution increases the risk of crystal deposits, filtering of the solutions before use is recommended. Most of the crystals can be removed from the paper surface by gentle brushing.

All treatments clearly delayed ink corrosion in comparison to no treatment. However, the question, how fast the corrosion process develops under normal storage conditions, is not yet answered satisfactorily. It is advisable, if aqueous treatment is considered, to wash ink-corroded papers sufficiently. Pre-wetting of ink-corroded



Figure 7. Discolouration of 12 days aged standard reference papers - clearly visible is the strong yellow discolouration of the magnesium bicarbonate treated paper, while the calcium bicarbonate and the calcium phytate / calcium bicarbonate treated papers are only insignificant yellowed in comparison to the untreated reference. Due to artificial ageing, the ink of all samples darkened with the exception of inks treated with magnesium bicarbonate. Tis inks changed to a lighter brownish colour.

papers (showing mechanical decay) using an alcohol like ethanol minimises mechanical decay during washing.

In order to achieve good protection against ink corrosion and exclude most side effects, calcium bicarbonate treatment or a calcium phytate/calcium bicarbonate treatment can be recommended.

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References

- 1 The non-bleeding iron test for iron(II) ions has been developed as a simple and rapid method to detect iron(II) ions. The indicator (bathophenanthroline) forms an intensely red-coloured complex with iron(II)-ions. Neither the complex nor the indicator is water-soluble; therefore there is no risk of bleeding during contact.
- 2 The following data are recent parameters (2/1999), provided by the Gemeentewaterleidingen Amsterdam, Afd. Waterqualiteitsbewaking: Na: 82-87 mg/l, K: 4,5-4,7 mg/l, Ca: 47-48 mg/l, Mg 8,6-8,9 mg/l, Al: < 0,003 mg/l, Fe: 0,01 mg/l, Mn: < 0,01 mg/l, Cu: 0,028 mg/l, free & total chlorine: 0 mg/l, chloride: 102-107 mg/l, sulphate: 52-55 mg/l, nitrate: 7,6 mg/l, carbonate: < 0,5 mg/l, SiO₂: 8,2-9,2 mg/l, pH 8,1 – 8,25, total Hardheit: 8,6 (D).
- 3 Papers treated with magnesium phytate appeared much whiter than the untreated reference and papers treated with magnesium bicarbonate in former testing series (Kolbe 1998). This could not be proved in case of calcium phytate under the present treatment conditions.
- 4 Sulphuric acid is formed during the formation of the ink complex. If iron sulphate and gallic acid was used to prepare the ink, an iron-gallate complex (black coloured) and sulphuric acid are consequently formed.

Keywords

paper, iron gall ink, ink corrosion, aqueous treatment, deacidification, chelating

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Birgit Reißland received her diploma in paper conservation from the State Academy of Art, Stuttgart, in 1997. Since 1996 she has been involved in the Ink Corrosion Project of the Dutch Institute for Cultural Heritage, Amsterdam, where she studied processes involved in ink decay as well as investigated the influences of active conservation measures.

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