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ARTICLE *in* CELLULOSE · DECEMBER 2008

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# Iron gall ink-induced corrosion of cellulose: aging, degradation and stabilization. Part 1: model paper studies

Antje Potthast · Ute Henniges · Gerhard Banik

Received: 9 January 2008 / Accepted: 23 June 2008  
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**Abstract** Cellulose in historic paper documents is often damaged by the writing media used, especially iron gall ink or copper pigments. Degradation induced by iron gall ink is suggested to be a synergistic process comprising both hydrolytic and oxidative reactions. These processes were studied on very low sample amounts according to the CCOA and FDAM method, i.e. by fluorescence labeling of carbonyl and carboxyl groups in combination with GPC-MALLS, respectively. This study focused on preventive means to stop the deterioration induced by iron gall ink of cellulose and to prevent further damage, keeping in mind that a suitable conservation treatment has to hinder both, hydrolytic and oxidative processes, at the same time. A combination of the complexing agent calcium phytate and calcium hydrogencarbonate in aqueous solution was proved to give optimum results. To gain insight into long term stability, an aging step was performed after treatment and different ink modifications were tested. Recording the molecular weight distributions and the carbonyl group content over time GPC analysis verified for the

first time the preventive effect of this treatment. This effect was not only seen for the ink-covered areas, but extended also to areas remote from the ink lines. Ink containing copper ions responded equally positively to the calcium phytate/hydrogencarbonate treatment as the iron gall ink papers did. Gelatine, sometimes used in a similar way due to an alleged cellulose-stabilizing effect did not have a beneficial influence on cellulose integrity when metal ions were present.

**Keywords** Iron gall ink · Carbonyl groups · Cellulose degradation · Fluorescence labelling · Molecular weight distribution · Historic papers · Model papers · Phytate · Gelatine

## Introduction

Paper as a writing and drawing support, mainly made up of the natural polymer cellulose, is generally subject to complex aging processes. Acidic hydrolysis is considered to be the predominant degradation pathway for cellulose in paper, but oxidative processes come into play when frequently used writing and painting media, such as metallo-gallate inks and copper containing pigments, have been used (Lewin and Mark 1997; Shahani and Hengemihle 1986; Williams et al. 1977). Ink-induced corrosion of cellulose is a primary threat for paper documents of all kinds, ranging from letters in archives to drawings

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in collections of graphic art, and prevention of further iron gall ink corrosion is a crucial issue in conservation science.

Historic metallo-gallate inks are typically composed of two main ingredients, iron sulphate salt—mostly ferrous sulphate, but other sulphates being present in trace amounts as well—and a vegetable tanning agent, commonly gallotannin extracts from gall apples. These inks are referred to as iron gall inks due to one of the main components of this type of inks. Depending on source and preparation, the iron sulphate also contained impurities, such as copper, zinc, manganese, aluminium and magnesium salts, establishing a complex system of different stabilizing and destabilizing metal ions (Kolar et al. 2003). As the stability of the iron gall ink complex is governed by the ratio between Fe(II) ions and tanning agent, the concentration of tannic and gallic acid in the chosen supply is of great importance. In natural sources (gall apples) the concentration of these components varies considerably, even within one species and also upon aging (Mitchell 1916). Additionally, all kinds of modifiers have been added to iron gall inks, usually gum Arabic as protective colloid and alcoholic liquids to improve extraction, but towards the end of the nineteenth century also hydrochloric acid was used (Bergerhoff et al. 1991; Zerdoun Bat-Yehouda 1983). Consequently, historic iron gall inks hardly represent reproducible systems which render studies into iron gall ink corrosion quite intricate.

Considering all the ingredients of iron gall ink, the question arises what the actual driving mechanism behind ink corrosion is. During the production of iron gall ink, acidic components are used preferably, and upon formation of the iron gall ink complex, sulphuric acid is released (Neevel and Mensch 1999b). Ideally, all iron ions should be bound in stable colour forming complexes, provided there are sufficient amounts of chelating agents, i.e. tannic acid, present. Such metallo-gallate inks are termed balanced inks. Due to the varying sources and materials, full complexation cannot be generally assumed, so that in most cases metallo-gallate inks are unbalanced. Therefore, free transition metal ions are expected to be present in the system and free to act in redox reactions leading to Fenton-type radical formation (Emery and Schröder 1974; Neevel 1995; Strlič et al. 2003).

The question of the driving force behind ink corrosion has an important implication on considerations for conservation treatments of damaged cellulosic objects. If the main mechanism is hydrolytic a deacidification treatment—as performed for paper based documents containing acid compounds to neutralize these acids and deposit an alkaline reserve as protection against future acid attack—should be able to stop or at least to slow down the degradation. By contrast, if oxidation was the driving force behind degradation, a simple deacidification would not be sufficient to stop oxidation (Hey 1981; Neevel 1995).

As synergistic effects between acidic hydrolysis and metal-induced oxidation have been suggested for both historic and model papers, reasonable treatment options should inhibit the two different degradation mechanisms similarly. To study the underlying degradation mechanisms two different types of ink, unbalanced iron gall ink and unbalanced iron gall ink plus copper sulphate were applied on model papers. A calcium phytate/calcium hydrogencarbonate treatment, as found to be successful (Hey 1981; Neevel 1995), was investigated as a means to stop and counteract iron gall ink corrosion. Basically the success of the treatment was monitored by an increase in pH (Banik et al. 2002; Neevel 1999a). Additionally, the influence of gelatine sizing was investigated as proteins are reported to possess cation-binding capacity that supposedly should help to immobilize metal ions and keep them from reacting (Barrett and Mosier 1995; Kolbe 2004).

## Material and methods

### Fluorescence labelling

Carbazole-9-Carbonyl-Oxy-Amine (CCOA) labelling of carbonyl groups was performed as described earlier (Potthast et al. 2003; Röhring 2002a, b).

### General analytics

Gel permeation chromatography (GPC) measurements used the following components: online degasser, Dionex DG-2410; Kontron 420 pump, pulse damper; auto sampler, HP 1100; column oven, Gynkotek STH 585; fluorescence detector TSP FL2000 (CCOA); multiple-angle laser light scattering

(MALLS) detector, Wyatt Dawn DSP with argon ion laser ( $\lambda_0 = 488$  nm); refractive index (RI) detector, Shodex RI-71. Data evaluation was performed with standard Chromeleon, Astra and GRAMS/32 software.

#### GPC method

The following parameters were used in the GPC measurements: flow:  $1.00 \text{ mL min}^{-1}$ ; columns: four PL gel mixedA LS,  $20 \mu\text{m}$ ,  $7.5 \times 300 \text{ mm}$ ; fluorescence detection:  $\lambda_{\text{ex}} = 290 \text{ nm}$ ,  $\lambda_{\text{em}} = 340 \text{ nm}$  (CCOA); injection volume:  $100 \mu\text{L}$ ; run time: 45 min. *N,N*-dimethylacetamide/lithium chloride (0.9% w/v), filtered through a  $0.02 \mu\text{m}$  filter, was used as mobile phase.

#### Standard deviations

The standard deviation for carbonyl group determination is below 5%, for the weighted average molecular weight approximately 5% and for number average molecular weight around 10%. These values are based on long-term determinations of standard pulps.

#### Model papers

Test papers were prepared of Whatman filter paper no. 1 containing almost pure  $\alpha$ -cellulose without sizing or fillers. Although the material does not entirely reflect historic rag paper, the changes at the cellulose of Whatman filter paper can be measured without having effects originating from hemicelluloses, residual lignin and other naturally occurring paper components. Samples with no ink application are referred to as reference papers.

On the test papers, iron gall ink was plotted with a Roland DXY-1150 plotter. The composition of the iron gall ink was 1.23 g of tannic acid (95% Aldrich), 1.05 g of iron (II) sulphate heptahydrate (Fluka) dissolved in 10 mL of gum Arabic solution ( $78.5 \text{ g L}^{-1} \text{ H}_2\text{O}$ ) (Fluka) and filled up to 25 mL with  $\text{H}_2\text{O}$ . This ink is abbreviated in the following as “OU”. To investigate the influence of copper ions, 7% of copper (II) sulphate pentahydrate (Fluka) has been added to some samples, this copper-containing iron gall ink being abbreviated “OK”.

## Treatment and aging

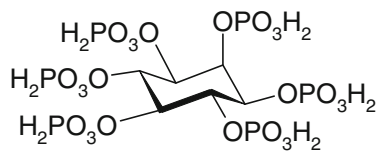
### Phytate treatment

To produce uniform oxidation of iron gall ink and paper, model sample paper was first submitted to mild pre-aging ( $70^\circ\text{C}$  and 50% relative humidity) for three days before further treatment (Kolar and Strlič 2000).

Half of the sample was treated with phytate, the other half remained as the reference. The treatment with calcium phytate/calcium hydrogencarbonate was performed according to Reißland (1999) using calcium carbonate (Merck), and phytic acid (Mitsui Chemicals) in solution at a pH of 5.9 (Fig. 1). The sample paper was immersed in a bath for 20 min, dried and sized with 1% gelatine solution using an airbrush. Besides this gelatine surface sizing being added to the dried paper after aqueous phytate treatment, one set of samples was sized with gelatine without any other treatment in order to see if any improvement solely due to the gelatine can be detected.

The samples with OU ink applied together with gelatine are referred to as “gelatine” in the following, and the samples with a phytate treatment performed on OU ink samples, are named “phytate”.

Except for the general preparation of the samples for dissolution no specific removal for the described components has been performed. As these general procedures include several aqueous and non-aqueous solvent exchange steps described earlier in the cited literature all these components will be removed during work-up. It was thoroughly tested if there was an influence of especially the gelatine, because it contains carbonyl groups. However, no influence could be measured, since the gelatine is completely dissolved during the activation procedure prior to cellulose dissolution in DMAc/LiCl and washed out. The presence of Fe and Cu ions did not show an effect on the CCOA labelling, which is done in Zn-acetate buffer. The ions itself if soluble are either washed out, if insoluble in water are filtered off prior to injection.



**Fig. 1** Phytic acid

## Accelerated aging

After treatment the treated and untreated samples were subject to accelerated aging, which was performed at 90 °C with the relative humidity cycling between 35% and 80% in a Vötsch Heraeus HC 0020 climate chamber. The paper was subsequently withdrawn from the climatic chamber after 0, 3, 6, 9, 12, and 18 days of accelerated aging. This approach allows not only the comparison of absolute values of molecular weight and carbonyl groups, but also a rough kinetic investigation, i.e. the comparison of rate constants if simple rate laws are applicable.

## Results and discussion

### Reference paper

The reference paper gives the degradation of the cellulose during aging without the action of any additives. The accelerated aging of the reference paper caused the expected degradation of the cellulose polymer. However, the degradation was still quite moderate. During accelerated aging a superposition of oxidation and hydrolysis was detected. The total amount of carbonyls is a sum of reducing end groups (REG) and carbonyls introduced by oxidation. The former contribution can be calculated from the number average molecular weight (Mn) and is indicative for cellulose hydrolysis. Glycosidic bond cleavage by hydrolysis will shorten the cellulose chain and concomitantly generate a “new” reducing end. Contrary to that, oxidation causes generation of carbonyls along the cellulose chain, which is generally not accompanied by simultaneous chain breakage. Especially with highly bleached samples of low overall carbonyl contents the calculation of  $DS_{REG}$  (degree of substitution of REG) often results in a “negative” number of oxidatively introduced units, since the calculated data for REG are in the same region as the total amount of carbonyl groups, as can be seen in Fig. 2. The estimation of the total amount of reducing ends from the number average molecular weight is an approximation based on the assumption that no REG are converted to acids and the determination of the Mn is correct. The error of measurement for Mn ranges around 10%. Still, this estimation approach is very useful when a decision

between a hydrolytic versus an oxidative degradation mechanism has to be made, especially when aging kinetics are recorded (cf. Fig. 2 bottom) and the slopes of carbonyl group formation are used as the respective measure.

This does not interfere with a kinetic description of the different processes. The formation of oxidized groups as well as the formation of REG follow a (pseudo)zero order rate law and can hence be directly compared.

From Fig. 2 it is obvious that the increase in the total number of carbonyl groups comprises roughly equal portions resulting from hydrolysis and oxidation, both processes had about the same  $k$ -values (ref. Table 1).

Figure 2 top presents the molecular weight distribution and the  $DS_{C=O}$  (degree of substitution of carbonyl groups) profile during accelerated aging. Until 12 days of aging, the decrease of Mw and Mn can be fitted according to a (pseudo) first order rate law (Fig. 2 left). Overall, the reference paper had the slowest increase in carbonyl values and a moderate decrease of molecular weight as expected.

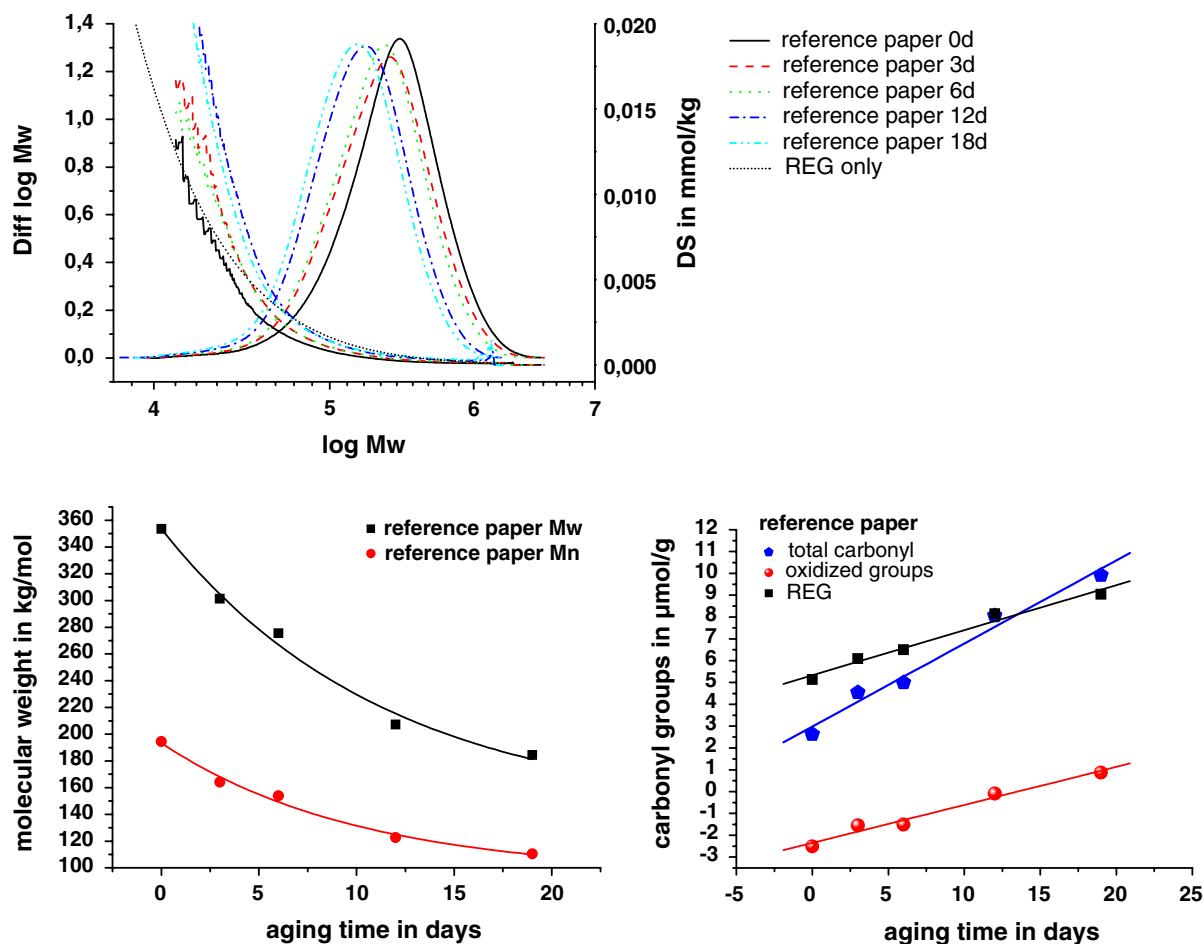
### Unbalanced ink

If an unbalanced gall ink was applied the total number of carbonyl groups increased more drastic. The rate of carbonyl formation was about ten times faster than compared to the reference paper. The degradation was dominated by hydrolytic chain cleavage, the rate of cellulose oxidation increased about five fold relative to the reference (Table 1).

The molecular weight distribution (MWD) showed some signs of accumulation of lower Mw degradation products after 12 days of aging, noticeable by the appearance of a shoulder on the low-Mw side (Fig. 3 top). The course of Mw and Mn over time (Fig. 3 left) did not follow a simple rate law anymore. The overall rate of degradation was much faster and reached alarmingly low Mw values of 37 kDa after 12 days of aging which corresponds to a DP around 200.

### Unbalanced ink containing copper ions

The addition of copper ions to the iron gall ink should even better simulate historical preparations and deterioration of paper as they are frequently found in inks



**Fig. 2** Reference paper without ink. Top: Molecular weight distribution (MWD) depending on the time of accelerated aging. Below left: Loss of weight (Mw) and number (Mn) average molecular weight depending on aging time. Below

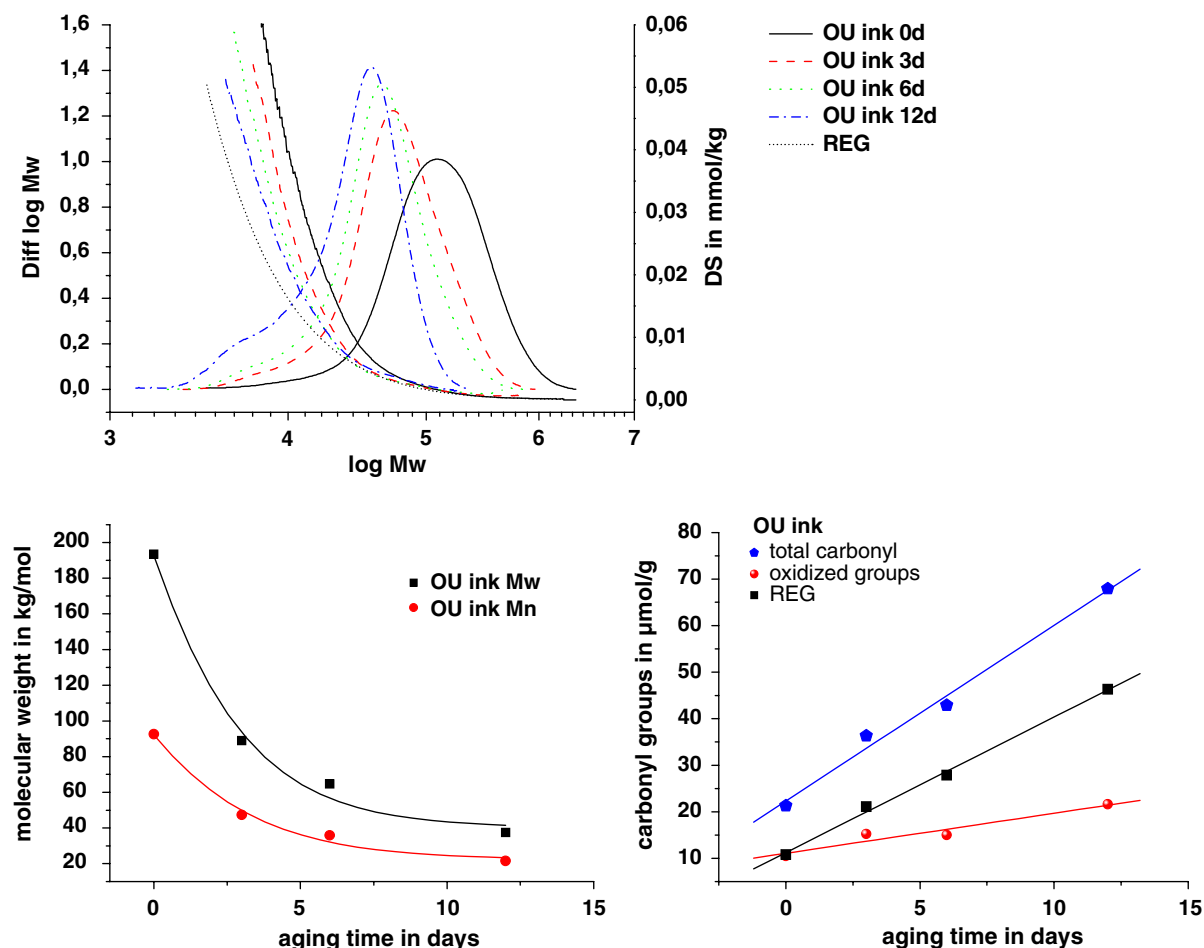
right: (pseudo)-zero order of carbonyl group formation: reducing end groups (REG) are indicative of hydrolytic processes, oxidized units are calculated from total C=O minus REGs and illustrate oxidative reactions

**Table 1** (Pseudo)-zero order rate constants in  $(\mu\text{mol g}^{-1} \text{d}^{-1})$ : overview of total C=O formation, oxidized units and hydrolysis (REG) for all samples studied

	Reference	Unbalanced ink (OU)	Unbalanced ink + $\text{Cu}^{2+}$ (OK)	Ink and gelatine	Phytate treatment
Total C=O	0.38	3.77	4.65	3.88	0.59
Oxidized units	0.17	0.86	1.57	0.82	0.39
REG	0.21	2.91	2.81	3.10	0.20

on ancient documents. Paper or cellulose deterioration induced by copper ions shows a significantly higher tendency to follow oxidative mechanisms; hence it was of interest if this behaviour could be simulated also in our model series with iron gall inks. From Table 1 it was evident that the rate of carbonyl group formation increased, whereas the rate of the hydrolysis stayed

about the same. It was clearly shown, that the addition of copper ions to the iron gall ink caused predominantly increased oxidation of cellulose without a significant influence on the hydrolytic degradation. Analyzing the MWD, we found a final Mw which was in the same order of magnitude as compared to the unbalanced iron gall ink without the addition of copper ions. However,



**Fig. 3** Unbalanced ink. Top: Molecular weight distribution (MWD) depending on the time of accelerated aging. Below left: Loss of weight (Mw) and number (Mn) average molecular weight depending on aging time. Below right: (pseudo)-zero

order of carbonyl group formation: reducing end groups (REG) are indicative of hydrolytic processes, oxidized units are calculated from total C=O minus REGs and illustrate reactions involving oxidation

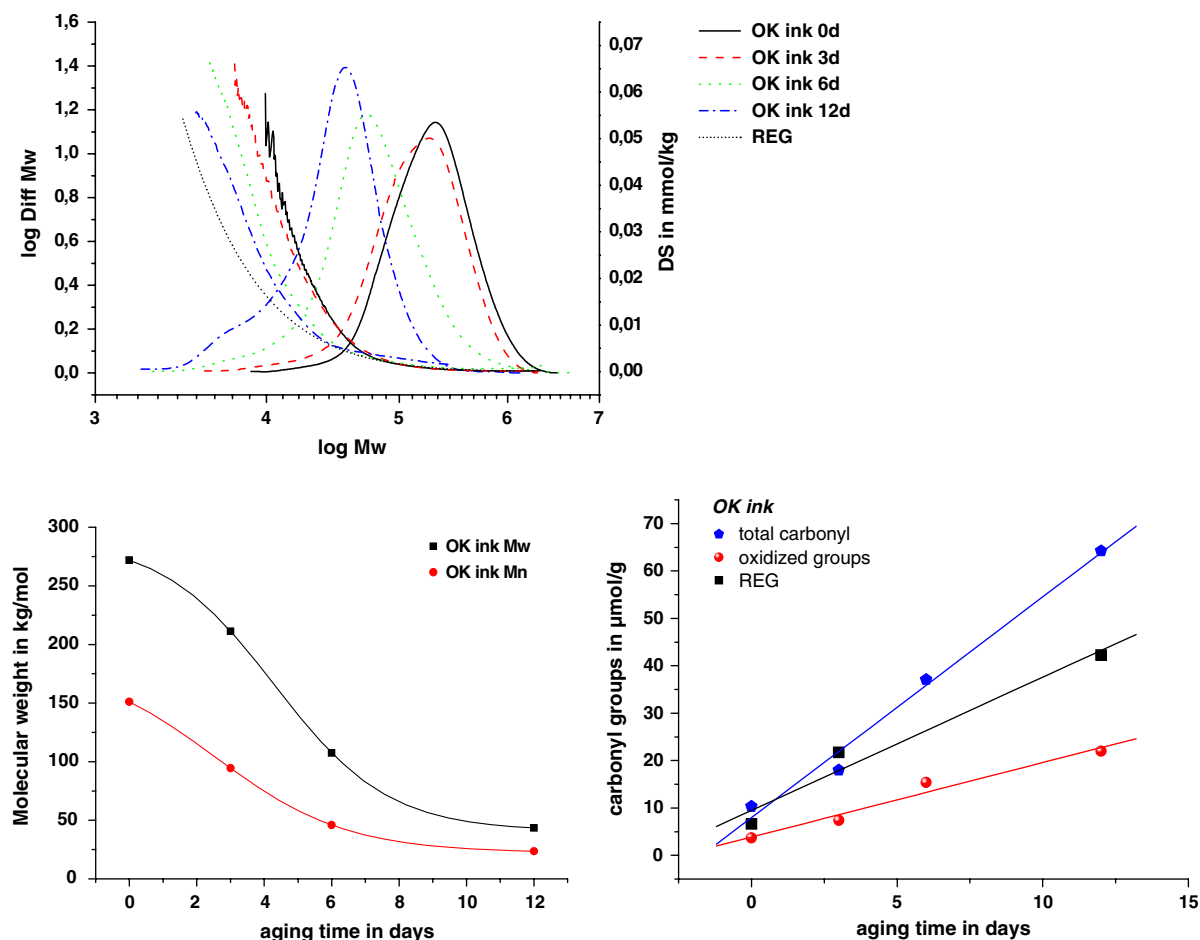
the course of degradation was first slowed down and subsequently accelerated (Fig. 4, left), and indicates a more complex reaction kinetics.

#### Addition of gelatine

Gelatine surface sizing was added to the dried paper after aqueous phytate treatment. Gelatine is believed to slow down iron gall ink corrosion as it reduces ion mobility and, good penetration provided, forms a protective layer between inks or pigments and paper carrier. Being a protein, gelatine may also show a stabilizing effect per se when applied to iron gall ink containing paper. A possible complexation

of metal ions by gelatine is discussed in that respect (Banik et al. 2002). Also, gelatine is often used as a resizing agent as part of the conservation treatment because parts of the original sizing are assumed to get lost during aqueous treatments. We applied gelatine alone (without phytate or phytate/CaHCO<sub>3</sub>) to detect any isolated effects of the sizing. Table 1 clearly shows the result: gelatine had no pronounced stabilizing effect on cellulose itself when iron gall ink is present. The rates of both oxidation and hydrolysis were in good agreement with those of the ink-covered sample. In Fig. 5 these conclusions are visualized giving the same parameters as in the figures above.





**Fig. 4** Unbalanced ink with addition of  $\text{Cu}^{2+}$ . Top: Molecular weight distribution (MWD) depending on the time of accelerated aging. Below left: Loss of weight (Mw) and number (Mn) average molecular weight depending on aging

time. Below right: (pseudo)-zero order of carbonyl group formation: reducing end groups (REG) are indicative of hydrolytic processes, oxidized units are calculated from total C=O minus REGs and illustrate oxidative reactions

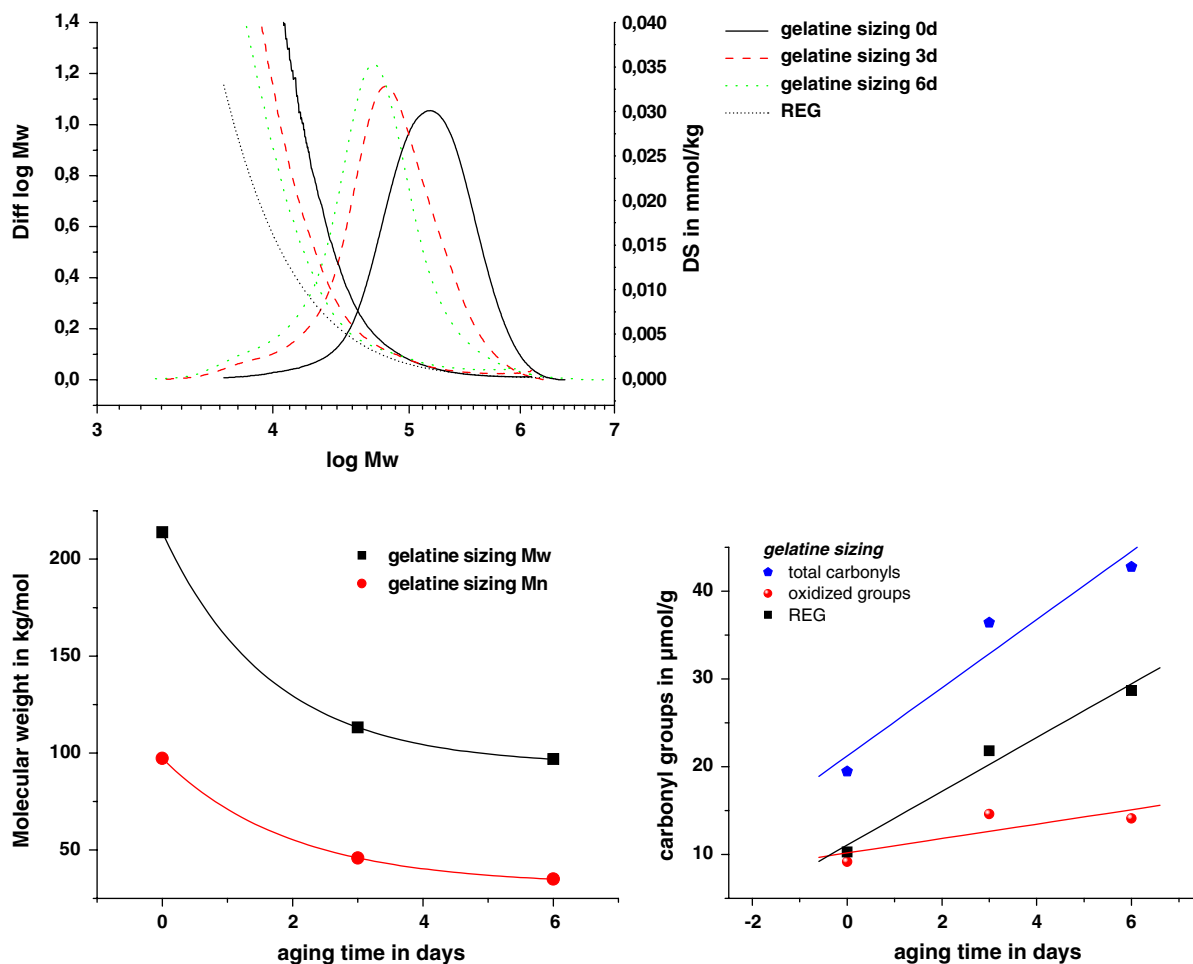
### Phytate treatment

The results of the unbalanced iron gall ink treated with the phytate solution were quite unexpected. The surprisingly good stabilization of the molecular weight is shown in Fig. 6, top. The shift of the MWD towards lower Mw was quite small when the severity of the conditions is taken into account and if we compare this outcome to the unbalanced iron gall ink. The total amount of carbonyls remained almost constant during the first 6 days of aging. After 12 days a relatively small increase from 16 to 24  $\mu\text{mol g}^{-1}$  carbonyl groups was observed—compared to about 70  $\mu\text{mol g}^{-1}$  reached in the case of the untreated ink sample. From Table 1 it can be concluded, that by phytate treatment the hydrolytic processes are

suppressed down to the level of plain reference cellulose, the overall carbonyl formation rate being only slightly higher than on those samples without ink application. In the case of phytate, we have to consider the rather difficult fit of the data (cf. Fig. 6, right).

Figure 7 summarizes the courses of carbonyl group development for all different samples upon accelerated aging, showing on the left side the total carbonyl group content, on the right side the amount of introduced oxidized functionalities (without the effect of REGs which were subtracted from the overall carbonyl content). For iron gall ink treated with calcium phytate the slope was parallel to that of the reference blank paper, indicating a successful inhibition of oxidation. Untreated inks exhibited a much steeper slope.





**Fig. 5** Unbalanced ink with the addition of gelatine. Top: Molecular weight distribution (MWD) depending on the time of accelerated aging. Below left: Loss of weight (Mw) and number (Mn) average molecular weight depending on aging

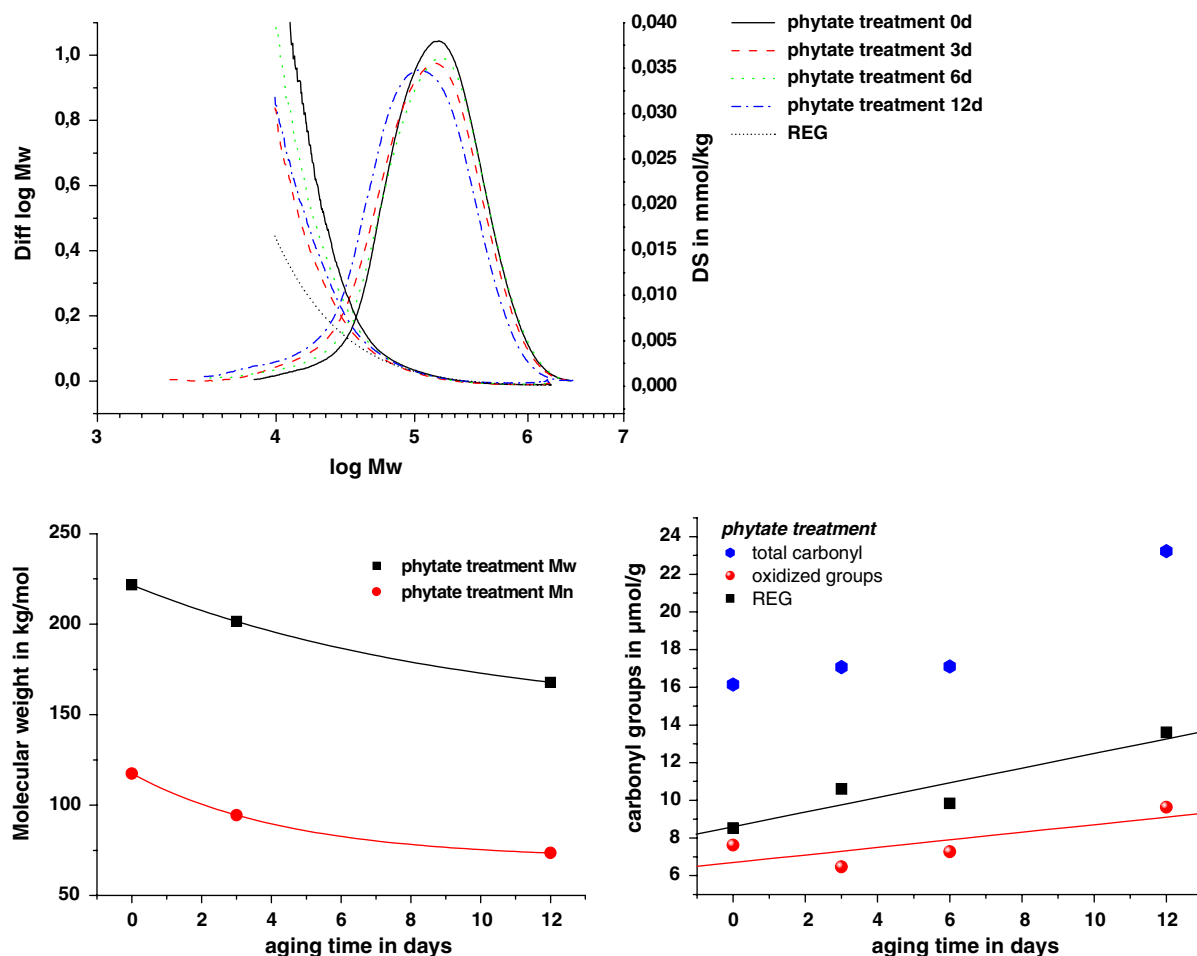
In Fig. 8 the Mw development in the course of accelerated aging is compared for all samples studied. For iron gall ink paper treated with calcium phytate the slope was even more flat than for blank reference paper, indicating the beneficial effect of the treatment also to the plain reference paper.

One important observation was the fact that even before accelerated aging, i.e. just by application of the different inks and treatments, the starting Mw was different. One explanation is an incipient degradation already during the application and pre-aging procedure. Also the period of natural aging between sample preparation and sample measurement might reasonably be assumed to have caused the pre-aging differences in Mw (Fig. 8).

time. Below right: (pseudo)-zero order of carbonyl group formation: reducing end groups (REG) are indicative of hydrolytic processes, oxidized units are calculated from total C=O minus REGs and illustrate oxidative reactions

An interesting feature of the phytate treatment consists in the preservation especially of long cellulose chains as demonstrated in Fig. 9. The shape of the MWD distribution was broadened by the phytate treatment, but there was no significant loss in higher molecular weight regions. This is especially important since the high Mw components of cellulose are mainly responsible for the required strengths properties of the material.

Figure 10 compares the relative rates for oxidation and hydrolysis underlining the conclusions above. The hydrolysis rates for gall-ink paper, copper-fortified gall ink paper and gelatine-sized paper were nearly the same, lying on a rather high level. A phytate treatment reduced the hydrolytic degradation down to the stage of



**Fig. 6** Unbalanced ink with phytate treatment. Top: Molecular weight distribution (MWD) depending on the time of accelerated aging. Below left: Loss of weight (Mw) and number (Mn) average molecular weight depending on aging

time. Below right: (pseudo)-zero order of carbonyl group formation: reducing end groups (REG) are indicative of hydrolytic processes, oxidized units are calculated from total C=O minus REGs and illustrate oxidative reactions

the reference paper (no ink or sizing). With regard to oxidative changes, addition of copper ions to unbalanced iron gall ink had a clearly negative effect. Gelatine sizing gave no improvement in comparison to the iron gall ink sample. Phytate treatment was also beneficial with regard to the avoidance of oxidative modifications of the cellulose: the amount of carbonyls introduced was significantly reduced being almost down to the value of untreated reference paper.

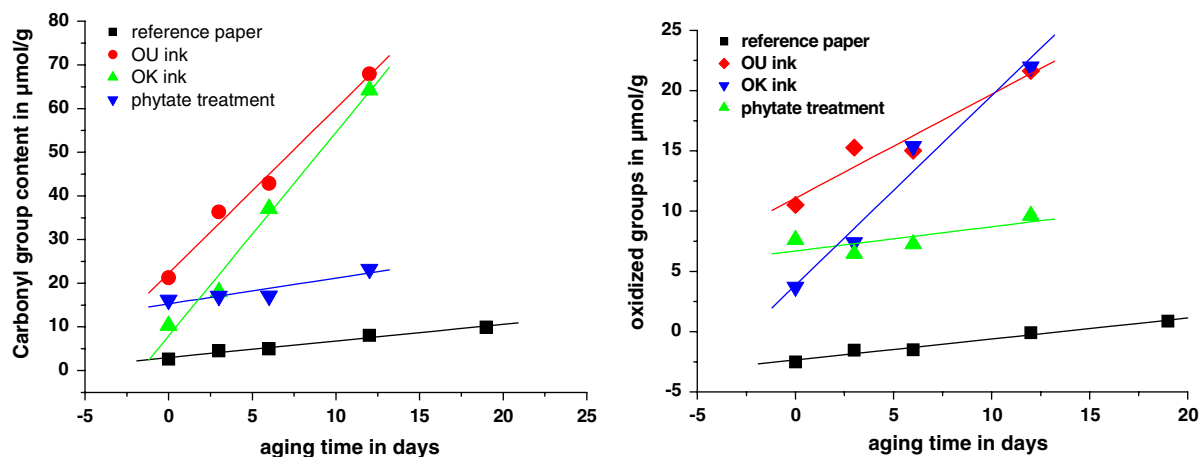
## Conclusions

Stabilization of the transition metal ion induced degradation of paper needs to address hydrolytic and

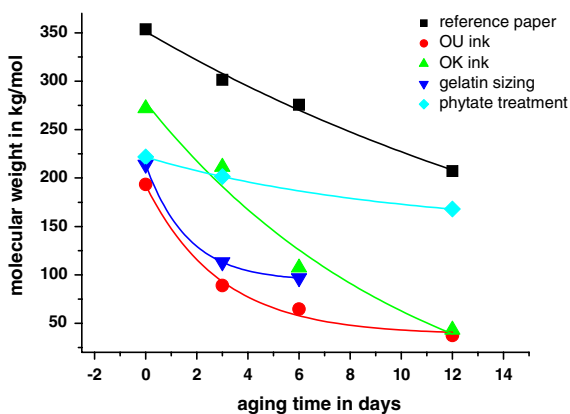
oxidative processes at the same time. Here, calcium phytate, a chelating agent, in combination with calcium hydrogen carbonate in order to neutralize acids was investigated.

Loss of molecular weight, i.e. hydrolysis of cellulose, was efficiently prevented by the phytate treatment. The rate of degradation in terms of molecular weight loss decreased, and the oxidative introduction of carbonyl groups slowed down considerably. The corresponding rate constants became comparable to those of paper without ink.

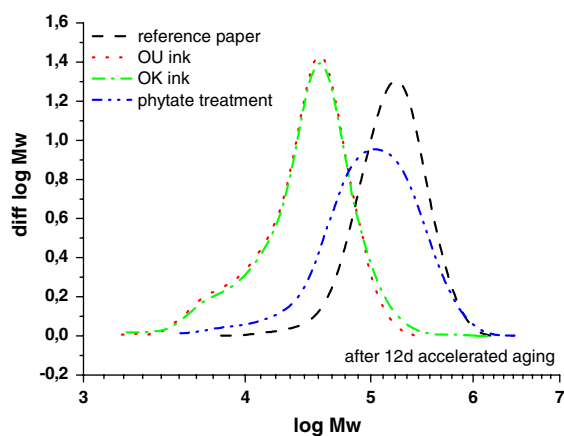
The phytate treatment was very effective in stabilizing unbalanced inks, containing both, iron and copper ions. It even showed a stabilization effect in the case of paper aging without metals. The



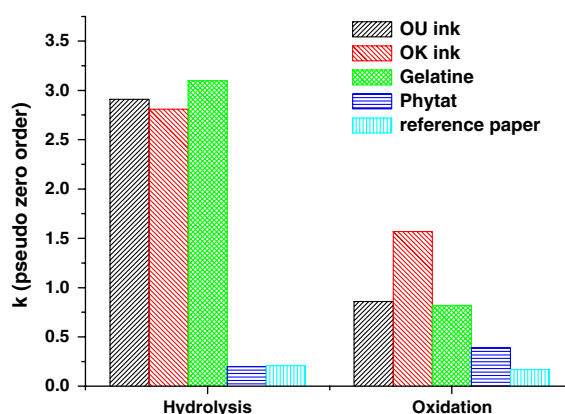
**Fig. 7** Development of carbonyl group content during accelerated aging. Left: Formation of total carbonyl groups. Right: Increase in oxidation



**Fig. 8** Development of molecular weight ( $M_w$ ) during accelerated aging



**Fig. 9** Molecular weight distribution of blank paper compared to treated and untreated iron gall ink samples. Calcium phytate treatment efficiently reduced molecular weight loss, especially also in high molecular weight regions



**Fig. 10** Comparison of hydrolysis and oxidation rates for the different modifications investigated

beneficial effect of phytate is attributed to a strong chelation of metal ions of different kinds, thus suppressing the generation of reactive radicals, in particular the detrimental hydroxyl radicals.

Comparing the data obtained we can conclude as follows: Iron gall ink on model paper caused both, hydrolysis and oxidation, the relation between the two processes depending on the type and composition of iron gall ink applied. In the present model case hydrolysis and oxidation proceeded nearly with the same rate. The addition of copper ions increased the rate of oxidation, but without having a significant influence on the rate of hydrolysis. The presence of gelatine had neither an effect on hydrolysis nor on oxidation of cellulose. The phytate treatment caused an enormous stabilization of the cellulose. The rate of

hydrolysis is decreased to the value obtained for plain cellulose without any ink present; the rate of oxidation was significantly slowed down as well.

The analysis of historic papers and naturally occurring degradation pathways—and the application of the knowledge gained with the model paper studies to this “real world case”—will be addressed in part 2 of this study.

**Acknowledgement** We would like to thank Dr. Sonja Schiehser for practical assistance. Dipl. Rest. Gesa Kolbe prepared the sample material, performed the treatment and conducted the accelerated aging procedure. We are grateful for the financial support by PAL GmbH, Leipzig, Germany and by the Austrian Science Foundation (FWF, Grant L188-N11).

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