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Studies into the Early Degradation Stages of Cellulose by Different Iron Gall Ink Components

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Summary: Selective fluorescence labelling of oxidized cellulose functionalities followed by GPC-MALLS was used to get a deeper insight into ink-induced degradation processes. As the method is very sensitive towards oxidation and molecular weight changes, slight variations at the very beginning of aging processes, e.g. during ink corrosion of cellulose, can be studied.

Five different ink modifications were applied on model papers and underwent mild accelerated aging at 55 °C and cycling humidity (7 days) followed by a short period of static humid aging at 80 °C (2 days). Pure ink constituents like tannic acid or iron sulphate do not result in the same degree of oxidation or chain scission as complete inks. Balanced ink degrades paper more than single compounds, but less than unbalanced inks. Interestingly, some degradation occurs already during or shortly after the application process of unbalanced inks on paper. It could be demonstrated that this oxidation proceeded in a rather high Mw area, while the subsequent aging steps affected predominantly regions of shorter cellulose chains.

Keywords: carbonyl and carboxyl groups; cellulose; degradation; fluorescence; gel permeation chromatography; ink corrosion; molecular weight; oxidation; transition metal chemistry

Introduction

Iron gall ink has been an extremely important and popular writing and drawing medium for several centuries. Central parts of the written European cultural heritage are laid down using this ink which is easy to produce. Iron gall inks have been prepared according to a broad variety of recipes. Its main ingredients, though recipes vary much, are iron sulphate and extractives from plant galls. These extractives contain tannins, which will form a deeply coloured complex with iron(III). In aqueous dispersion this compound is known as iron gall ink. The iron gall complexes are mainly immobile while other ink components, e.g. sulphuric acid, may migrate into the surrounding paper.[1]

Regardless its broad usage this ink has also a considerable degrading influence on paper and cellulose that has been known for a long time. A conference in St. Gallen in 1898 is considered to be the starting point of systematic scientific research into this topic.[2–3]

As more observations were added, and knowledge on the phenomenon of iron gall ink corrosion was gained, more emphasis was put on the conclusion that iron gall ink corrosion seems to be a system with two contributing effects: acid hydrolysis due to sulphuric acid that is liberated during the formation of the iron gall complex, and transition metal ion catalyzed autoxidation triggered by iron ions.[4] Research came to the conclusion, that only so-called balanced inks – with an equilibrated molar ratio between iron ions and tannic acid of

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3.6 : 1 – will theoretically form a non-corrosive writing media. As recipes for iron gall ink preparation varied a lot, all kinds of unbalanced ratios, mostly containing excess iron ions, will occur in historic documents, leading to iron gall ink corrosion.[5]

The predominant aging pathway of cellulose and therefore of paper is hydrolytic chain scission. This was confirmed in model studies testing different humid aging conditions. Purely hydrolytic scission chemistry is described by the formation of one additional carbonyl group per chain scission, with no significant increase in carboxyl groups.[6]

There is not much literature explicitly addressing the analysis of oxidative or hydrolytic reaction pathways in the iron gall ink system and the contribution of the single ink components to the degrading action. Contrary to that, there are many investigations dealing with the oxidative potential of transition metal ions. The influence of selected metal traces on the colour and colour stability of purified cotton linters has been investigated by Czepiel in the 1960's.[7] In the 1970's Emery and Schroeder investigated the oxidation of cellulose and hemicelluloses in the presence of iron and found that, contrary to other reports, the reaction was favoured in acidic conditions.[8] Especially the negative influence of iron and copper ions on the permanence of paper has been worked on extensively.[9–12] Recent research extended on the catalytic activity of Cd(II), Co(II), Cr(III), Mn(II), Ni(II), and Zn(II) in addition to Cu(II) and Fe(III). At neutral pH, Cu(II) was found to be the most active cation, while Cd(II) and Zn(II) did not exhibit any catalytic activity. Small amounts of Zn(II), Co(II) and Mn(II) will exhibit pro-oxidative effects.[13]

Tannic acid, a polyphenolic substance, was investigated mostly in the context of food chemistry. Tea polyphenols were found to be powerful antioxidants.[14–15] Also, the pro-oxidative effects of gallic acid in Fenton-type systems containing H_2O_2 and Fe-(III) at different pH and temperature have been addressed. The overall effect was found to be dependent on the ratio of gallic acid and Fe(III) in the reaction medium.[16]

On paper, the volatile organic compounds (VOC) of different iron gall ink ingredients, separate and combined, have been analyzed. The authors came to the conclusion, that tannic acid and gum Arabic alone do not produce VOCs, while their production is observed when only sulphuric acid and ferrous sulphate are present. Most VOCs are detected when iron gall ink containing all ingredients has been used.[17] This may be regarded as a proof of synergistic effects in the iron gall ink corrosion system.

Mostly, this synergistic effect has been concluded from the fact that combined treatments, i.e. treatments that address acid hydrolysis by deacidification and autoxidation by adding chelating agents, appear to be more successful in slowing down iron gall ink corrosion than treatments on a deacidification basis only. Phytic acid as a chelating agent has been used in this context with good results.[18–20]

In order to investigate the influence of different ink ingredients on ink corrosion and to find out about the supposed synergistic effects, five different ink modifications were prepared and printed on model papers. Molecular weight, carbonyl and carboxyl groups were determined before, in the course, and after accelerated aging, with a special focus on the first days of aging.

Methods and Material

Labelling

Carbazole-9-carbonyloxyamine (CCOA) labelling of carbonyl groups was performed as described earlier.[21–23] Fluorenyl diazomethan (FDAM) labelling of carboxyl groups was performed as described by Bohrn.[24]

General Analytics

Gel permeation chromatography (GPC) measurements used the following compo-

Table 1.
Overview of investigated ink modifications (amount of substances needed to produce 25 mL aqueous solution).

Ink-Type		Composition
Balanced ink	OA	Iron(II)sulphate (1.05 g), tannic acid (1.7 g), gum Arabic (0.79 g)
Unbalanced ink	OU	Iron(II)sulphate (1.05 g), tannic acid (1.24 g), gum Arabic (0.79 g)
Copper ink	OK	Iron(II)sulphate (0.998 g), copper sulphate (0.053g), tannic acid (1.23 g), gum Arabic (0.79 g)
Tannic acid	OT	tannic acid (1.23 g), gum Arabic (0.79 g)
Iron(II)sulphate	OE	Iron(II)sulphate (1.05 g), gum Arabic (0.79 g)

nents: online degasser, Dionex DG-2410; Kontron 420 pump, pulse damper; autosampler, HP 1100 column oven, Gynkotek STH 585, fluorescence detector TSP FL2000 (CCOA) and Agilent FLD G1321A (FDAM); 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 mL/min; columns, four PLgel mixed-A LS, 20 μm, 7.5×300 mm (Polymer Laboratories); fluorescence detection, $\lambda ex = 290$ nm, $\lambda em = 340$ nm (CCOA), $\lambda ex = 252$ nm, $\lambda em = 363$ nm (FDAM); injection volume, 100 μL; run time, 45 min. *N,N*-dimethylacetamide/lithium chloride (0.9% w/v), filtered through a 0.02 μm filter, was used as mobile phase.

Test Papers

Test papers were prepared of modern handmade paper composed of linen and flax fibres without sizing or fillers. On this paper, five different modifications representing either iron gall inks or their constituents have been plotted on using a Roland DXY-1150 plotter. Two of these modifications are single constituents of iron gall ink, i.e. they only consist of one iron gall ink compound. These inks are referred to as iron(II) sulphate (OE) and tannic acid (OT). Three inks are composed of all constituents, but having different ratios between metal ion content and tannic acid content. They are referred to as balanced ink having the ideal ratio of 3.6 : 1 between iron ions and tannic acid (OA-ink), unbalanced ink (OU ink), and unbalanced ink containing additional copper ions (OK-ink). For detailed composition see Table 1.

Accelerated Aging

To observe the development of degradation, the different samples with single

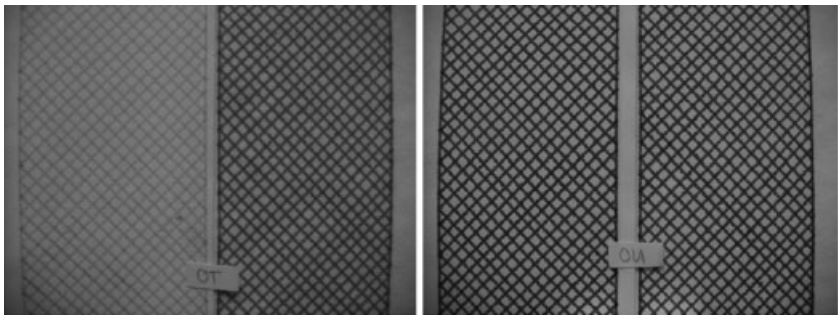

Figure 1.
Left: Tannic acid (OT) experienced most visual changes during aging. It turned from a pale yellow into intense greenish yellow. Right: for all inks (OA, OK and OU) only slight visual changes were observed. Typically, these inks turn from a slightly bluish black into a more brownish black.

ingredients respectively ink modifications have been subjected to accelerated aging. The aging procedure started with one day of pre-aging to build up an even state of oxidation.[25] The following accelerated aging procedure has been divided into two phases. The first phase was designed to encourage mobile compounds to start migration processes as observed in natural aging. Therefore aging conditions were set on 55°C and cycling humidity from 35% - 85% - 35% relative humidity (one cycle = 6h). After this period of cycling humidity, the second phase aging mode was changed to static conditions at 80 °C and 65% relative humidity for two days.

Based on previous research, this period is considered to be sufficient to study the starting period of iron gall ink corrosion. Samples were drawn after every single aging day.

Sampling. Each paper has an area covered with one of the five modifications described above in Table 1 and an edge area that is not influenced by the applied substances. In order to study corrosion processes, one sub sample per sample was always taken from the covered areas and compared to a second sub sample that was taken from the edge area, as far away from the visible pattern as possible. As the paper material from the edge area is supposed to be the same for all five samples, a mean (referred to in the following as ''paper mean'') was calculated to compare covered and non-covered areas with each other. Using this sampling protocol the influence of the chosen aging procedure on cellulose and on cellulose + ink or ink ingredient can be studied.

Results and Discussion

Visual Analysis

The first observations in the course of accelerated aging are colour changes. As a rule of thumb, single ingredients (OE and OT) will have most obvious colour changes from a rather pale colour into a more intense and dark one. Contrary to that, all inks (OA, OU and OK) do not suffer from pronounced colour changes; they rather change in terms of hues (Figure 1).

When it comes to changes in hydrophobicity and observable migration (tested through application of a defined water droplet), most changes are again observed for single ingredients (OE and OT) applied on paper. Inks (OA, OU and OK) are quite hydrophobic from the beginning, while water repellence decreases considerably in the case of OT (tannic acid, single ingredient).

Oxidative Changes

CCOA and FDAM fluorescence labelling of oxidized cellulose functionalities permitted a detailed study of oxidized structures in model papers with single ingredients or different ink modifications on it. CCOA is able to record already very small changes; hence the investigation of the early stages of corrosion at model papers becomes feasible. Thanks to the high sensitivity, also the influence on oxidation and chain scission of comparatively low temperatures during accelerated aging could be analyzed.

In Table 2 all data regarding carbonyl group contents are shown. The carbonyl group content of the paper from the edge area that is not affected from single ink ingredients or ink modifications increased from 3.4 μmol/g to 4.1 μmol/g. This is not regarded as significant oxidation in the paper itself after 7 + 2 days of accelerated aging. The overall effect on carbonyl group development was small. No sample exceeded 10 μmol/g carbonyl group content, which is still a comparatively low value.

To compare the influence of the single ink ingredients and the different inks, a mean of the paper taken from the edge of the sample material that was not influenced by any applied substance was calculated and the areas affected by an application contrasted to it (Figure 2).

Evidently, in OT-samples almost no oxidation occurs at all. The detected amounts of carbonyl groups are more or less equal to the paper mean. The other

Table 2.
Carbonyl group content after determination with CCOA fluorescence labelling for sample material with different ink modifications compared to edge area (paper mean: n = 5).

	OA: Balanced ink [μmol/g]	OU: Un-balanced ink [μmol/g]	OK: Copper sulphate ink [μmol/g]	OT: Tannic acid [μmol/g]	OE: Iron sulphate [μmol/g]	Paper mean [μmol/g]
2a (reference)	5.3	9.0	7.2	2.9	5.0	3.4
2b (pre-aging)	5.6	8.7	8.1	5.0	8.3	3.3
2c (1d cycling)	6.0	7.3	6.0	3.2	4.6	3.3
2d (2d cycling)	6.8	7.6	5.9	2.9	4.8	3.6
2e (3d cycling)	6.7	6.9	5.9	3.0	4.8	3.6
2f (4d cycling)	6.3	8.9	6.7	3.5	6.3	3.5
1a (5d cycling)	7.4	5.8	5.5	3.5	4.8	3.5
1b (6d cycling)	7.8	7.7	5.9	3.4	4.4	3.4
1c (7d cycling)	6.1	6.5	6.3	3.4	4.1	3.4
1d (7d cycling + 1d static)	7.9	6.7	6.3	4.2	4.8	3.6
1e (7d cycling + 2d static)	8.2	9.9	9.4	4.4	5.7	4.1

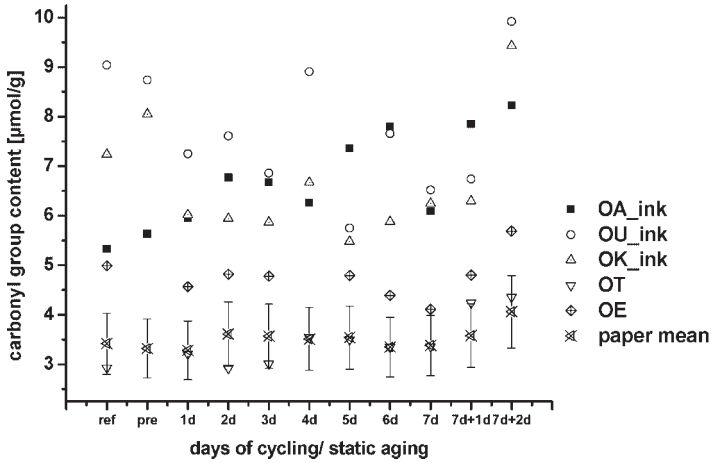

Figure 2.
Formation of carbonyl groups in reference data, pre-aging and after 1, 2, 3, 4, 5, 6 and 7 days of cycling aging + 1 and 2 days of static aging (removal of three outliers). Paper mean was taken to compare the influence of ink ingredients or inks to aging without the influence of the ink ingredients or inks, standard deviation was calculated for paper without any applied substance only (paper mean: n = 5, average SD = 18%[1]

single ingredient, OE-sample, is slightly more oxidized, but development of carbonyl groups is still parallel to paper mean and OT-samples.

All three inks show more oxidation than single ingredients. One important observation is the non-homogeneity in carbonyl group development, mainly of ink samples. The data do not follow a straight line, but a more complicated pattern of increasing and decreasing carbonyl group content during aging. We assume that this variation is due to irregularities during plotting. Additionally, the model paper is not sized, and a uniform ink application on unsized paper is difficult to obtain. Differences in ink absorption occurring in the hand made model paper are not levelled out, and therefore some areas might have been soaked with more ink than others, leading to irregular overall degradation.

Another observation is the instant oxidation occurring with inks – directly after ink application. Especially with unbalanced ink (OU-ink) and unbalanced ink containing copper (OK-ink) this effect is

[1]The large standard deviation is due to averaging 5 papers not due to the applied method.

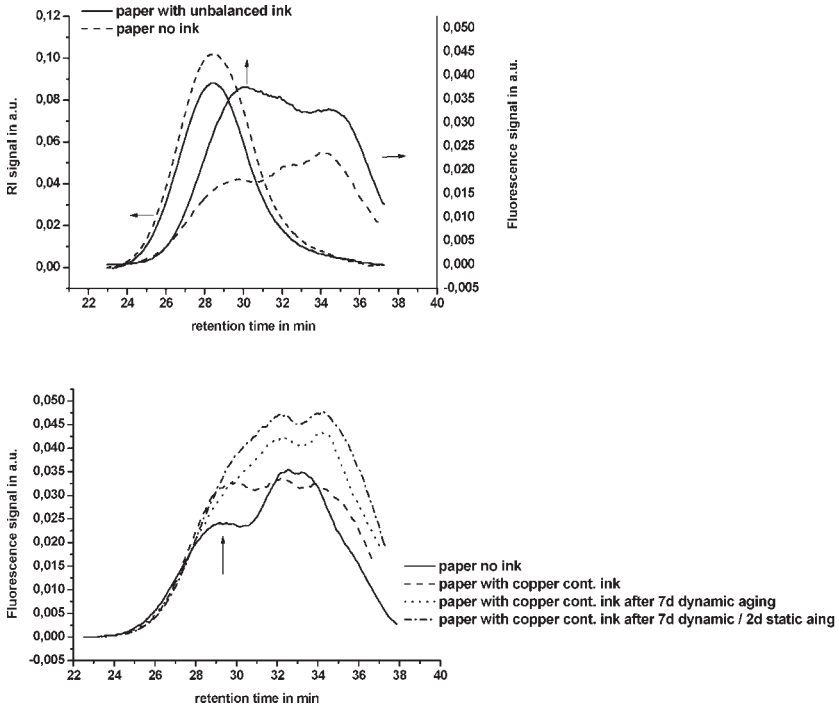

Figure 3.
Top: RI and fluorescence signal (corresponding to carbonyl groups) for paper with and without two unbalanced ink modifications; the fluorescence signal is increased at retention times around 29 min, corresponding to an MW of 200 kg/mol after ink application (see arrow). The same effect is also observed when copper is present (bottom): in the subsequent course of accelerated aging the maximum of the fluorescence peak shifts slightly from higher to lower molecular weight regions.

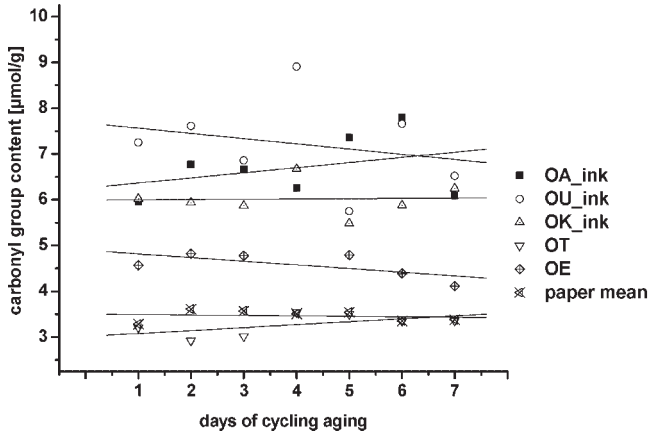

Figure 4.
Kinetics of carbonyl group development covering cycling aging only (pre-aging steps 2a and 2b not shown, removal of outliers). Paper mean was taken to compare the influence of ink ingredients or inks to aging without the influence of the ink ingredients or inks (paper mean: $n = 5$). No significant increase in carbonyl group content can be observed after seven days of cycling aging.

Table 3.
Summary of k-values for assuming a (pseudo)-zero rate law of all ink modifications plus paper mean. During cycling aging no significant increase or decrease can be observed. After static aging, especially inks exhibit an increase in carbonyl group content, while OE and OT can still be compared to paper mean.

	OA: Balanced ink [μmol/g]/d	OU: Unbalanced ink [μmol/g]/d	OK: Copper sulphate ink [μmol/g]/d	OT: Tannic acid [μmol/g]/d	OE: Iron sulphate [μmol/g]/d	Paper mean [μmol/g]/d
Cycling aging (2c-1c)	0.1	−0.1	0.0	0.1	−0.1	0.0
Static aging (1c-1e)	1.1	n.d.	n.d.	0.5	0.8	0.5

very pronounced, leading to an increase of carbonyl groups by a factor of 3 without any accelerated aging. There is obviously some natural aging due to the time that passes between sample preparation and measurement. Nevertheless, as the paper without any applied substance does not show any changes, nor do single ingredients, some cellulose structures respond immediately to ink application. The amount of carbonyl groups then decreases again after pre-aging. As with these samples also a noticeable loss in molecular weight (see later) occurs after ink application, ''weak spots'' within the cellulose backbone must have undergone an instant degradation. However, the loss in Mw is not solely responsible for the increase in carbonyl groups, also additional oxidation occurs. In order to study where this immediate oxidation takes place, the fluorescence and the RI-signal were plotted against retention time (Figure 3). A bimodal function was obtained for inked paper and a trimodal function for paper only. The fluorescence signal detects that oxidation mainly occurs in higher molecular weight regions of about 200 kg/mol for inked paper samples (Figure 3, up arrows). This phenomenon was observed for both unbalanced inks. In the course of accelerated aging, the bimodal fluorescence function shifts more and more to an equal distribution between higher and lower molecular weight regions, thus oxidation in lower molecular weight regions gains more importance.

As two different aging steps have been used, a closer insight on aging kinetics can be gained when looking at the different aging procedures separately. In Figure 4 the carbonyl group development is plotted against cycling aging time. All data have been fitted according to a (pseudo)-zero

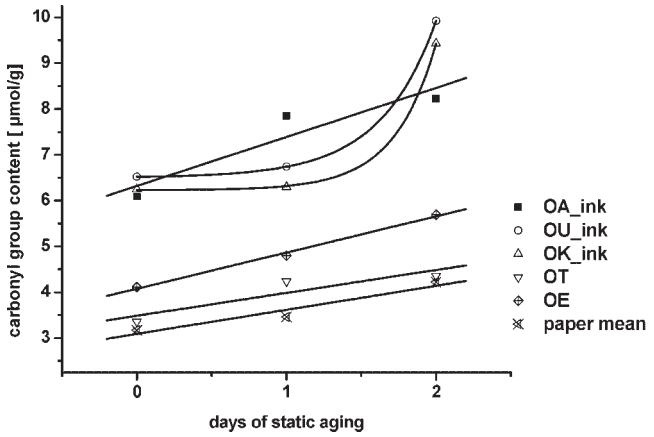

Figure 5.
Kinetics of carbonyl group development covering static aging only. Paper mean was taken to compare the influence of ink ingredients or inks to aging without the influence of the ink ingredients or inks (paper mean: n = 5). Especially for unbalanced ink (OU-ink) and unbalanced ink containing additional copper ions (OK-ink) there is an exponential increase of carbonyl group content.

rate law. From graphical and numerical analysis it is obvious that during the first seven days of aging no significant oxidation takes place in all samples (Table 3).

A detailed look at data after cycling aging reveals that most increase in oxidation for the observed period of aging obviously occurred during static aging (Figure 5). In this phase, samples start to diverge. In paper mean, OE-samples and OT-samples no strong development of carbonyl groups takes place, but in all three ink-samples the carbonyl group content is increased. While OA-ink can still be considered to behave according to a (pseudo)-zero order rate law, this is no longer applicable to OK-ink and OU-ink samples. Within the relatively short period of two additional aging days, both inks, OK and OU, have almost doubled their carbonyl group content.

In Table 3 the kinetic results for carbonyl group development are summarized. For the paper mean the k-value of static aging is 0.5 [μmol/g]/d, OT-samples have a similar value, OE-samples have a slightly stronger increase in carbonyl groups. OK-ink and OU-ink cannot be treated according to the same rate law.

The fact that some degradation takes place immediately after ink application while there are no pronounced changes during a quite long period of accelerated aging using cycling humidity can be interpreted as a deterioration process that is divided in at least two phases: a fast initial reaction and a slower induction phase. The occurrence of oxidation is furthermore strongly linked to the temperature. As soon as the temperature was increased in the second aging phase, the oxidation proceeded faster, at least for unbalanced ink and unbalanced ink containing copper ions.

The development of carboxyl groups was only followed on selected examples. A kinetic approach was not feasible with these data. Again, paper mean was calculated and the modifications were compared to it (Table 4). As for carbonyl groups the average carboxyl group content of the paper mean does not change significantly in the course of accelerated aging; there is only a slight tendency for carboxyl group decrease. For carboxyl group development, none of the inks shows a clear trend. In contrast to that, single ingredients changed the carboxyl group content of the cellulose. OE-samples seem to experience at least some kind of further oxidation to carboxyl groups. This behaviour is neither reflected in their carbonyl group development nor in other iron sulphate containing inks where un-reacted iron ions could have the same effect, i.e. promotion of further oxidation. Opposite to that, the amount of carboxyl groups is slightly decreased in OT-samples.

Both methods, CCOA and FDAM yield molecular weight distribution and molecular weight averages. For further discussion only the average molecular weight (Mw) obtained in the CCOA labelling procedure was used.

For the paper mean from the edge area, the accelerated aging reduces Mw from 306 kg/mol to 274 kg/mol (Table 5). During cycling humidity aging the original value is largely maintained, only after static aging a stronger decrease takes place.

For OA-ink, OE- and OT-samples the results are quite inhomogeneous. Again, like for carbonyl group development, inhomogeneous application might be an explanation for the irregular patterns observed.

Table 4.
Carboxyl group content after determination with FDAM fluorescence labelling for sample material with different ink modifications compared to paper without ink application (paper mean: n = 5).

	OA: Balanced ink [μmol/g]	OU: Unbalanced ink [μmol/g]	OK: Copper sulphate ink [μmol/g]	OT: Tannic acid [μmol/g]	OE: Iron sulphate [μmol/g]	Average paper [μmol/g]
2a (reference)	16.0	17.2	15.4	17.6	15.5	17.0
1c (7d cycling)	17.4	16.6	16.8	15.9	15.3	16.9
1e (7d cycling + 2d static)	16.8	17.0	16.4	14.7	18.8	16.0

Table 5.
Molecular weight average (Mw) after determination with CCOA fluorescence labelling for sample material with different ink modifications compared to paper without ink application (paper mean: n = 5).

	OA: Balanced ink [kg/mol]	OU: Unbalanced ink [kg/mol]	OK: Copper sulphate ink [kg/mol]	OT: Tannic acid [kg/mol]	OE: Iron sulphate [kg/mol]	Paper mean [kg/mol]
2a (reference)	301	265	267	335	306	306
2b (preaging)	357	265	265	306	n.d.	307
2c (1d cycling)	366	266	288	295	353	316
2d (2d cycling)	313	269	255	302	342	319
2e (3d cycling)	331	246	275	n.d.	369	313
2f (4d cycling)	347	253	265	277	325	306
1a (5d cycling)	338	233	266	270	285	303
1b (6d cycling)	310	230	254	282	376	315
1c (7d cycling)	348	210	240	286	367	304
1d (7d cycling + 1d static)	303	207	276	238	341	299
1e (7d cycling + 2d static)	291	188	224	276	276	274

Table 6.
Summary of rate constants k for all ink modifications and paper mean for decrease of molecular weight.

	OA: Balanced ink [kg/mol]/d	OU: Unbalanced ink [kg/mol]/d	OK: Copper sulphate ink [kg/mol]/d	OT: Tannic acid [kg/mol]/d	OE: Iron sulphate [kg/mol]/d	Paper mean [kg/mol]/d
Cycling aging (2c-1c)	−1.9	−9.2	−5.6	−2.9	0.9	−1.9
Static aging (1c–1e)	−28.1	−11.0	−8.2	n.d.	−45.2	−14.9

Nevertheless, the single ingredients and balanced iron gall ink (OA-ink) do not cause more decrease of molecular weight in the course of aging than the paper mean experiences. In contrast to that, there is a significant decrease in Mw in both unbalanced inks, OU and OK, the final value being at 188 kg/mol respectively 224 kg/mol (Figure 6). Interestingly, their Mws have decreased immediately after ink application, which leads to the suggestion that during application of unbalanced inks the observed oxidation is accompanied by a loss in molecular weight as well. A similar behaviour was observed also in previous studies.[26]

When studying the kinetics of molecular weight decrease during cycling aging, a

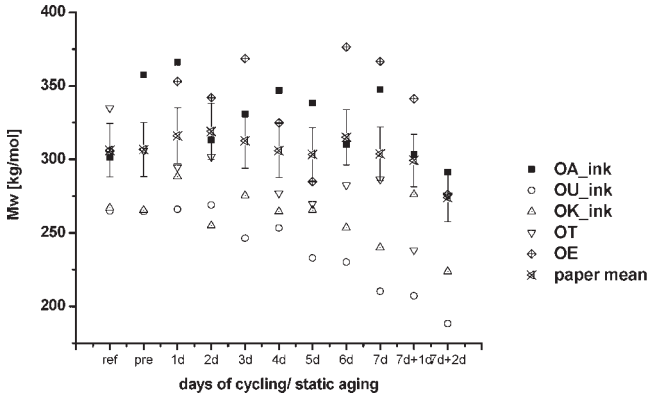

Figure 6.
Molecular weight data of reference, pre-aging and after 1, 2, 3, 4, 5, 6 and 7 days of cycling aging + 1 and 2 days of static aging (removal of outliers). Paper mean was taken to compare the influence of different ink ingredients or inks to aging without the influence of the ink ingredients or inks, standard deviation was calculated for paper without any applied substance only (paper mean: n = 5, SD without aging = 6%).

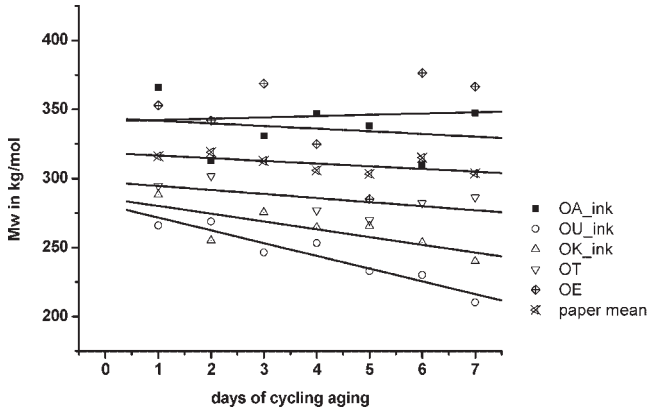

Figure 7.
Kinetics of molecular weight development covering cycling aging only (pre-aging steps 2a and 2b not shown). Paper mean was taken to compare the influence of different ink ingredients and inks to aging without the influence of ink ingredients and inks. Cycling aging leads to a decrease in molecular weight, especially for unbalanced ink (OU-ink) and unbalanced ink with copper ions added (OK-ink).

slight, but constant decrease in Mw of unbalanced ink modifications can be observed from the first day of aging on (Figure 7). Cycling aging obviously influences the molecular weight in a more pronounced way than compared to oxidation, i.e. hydrolysis slightly dominates the first period of aging for unbalanced inks.

Static aging increases the rate of chain scission for all modifications, but most strongly for OA-ink and OE-samples, followed by the paper mean that is used as a reference material. Interestingly, excess of metal ions in OK- and OU-inks caused less chain scissions than observed in paper mean. However, excess of iron ions as a single ingredient (OE) gave a considerable hydrolytic degradation, obviously due to a limited buffering capacity.

Conclusion

In summary, after two periods of accelerated aging, only minor oxidation took place for the model paper without any applied substance on it. Some decrease in molecular weight occurred, with an accelerated rate

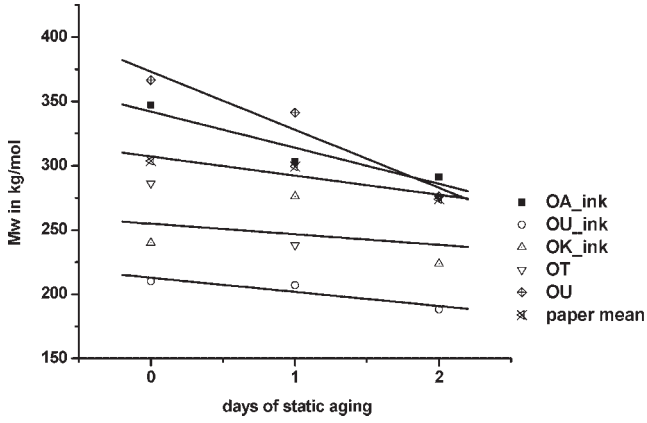

Figure 8.
Kinetics of molecular weight development covering static aging only. Paper mean was taken to compare the influence of ink ingredients or inks to aging without the influence of the ink ingredients or inks.

for static aging. For the paper from the edge area without any substance applied on it, only hydrolytic chain cleavage could be detected. Obviously, the chosen aging was a very mild one, which meets the intention to study the very beginning of cellulose degradation due to single ink ingredients and different iron gall inks.

A synergistic effect of simulated iron gall ink corrosion on model papers has been proven. Single ingredients (only iron sulphate respectively only tannic acid) will yield less oxidized functionalities. Considering chain scission, tannic acid applied on paper will prevent loss in Mw to a certain extent. Chain scission increases when iron sulphate is applied on paper.

All observed kinetics also support the thesis of the decreased degradation power of balanced inks, like in ink modification OA. Balanced ink will degrade cellulose to a greater extent than single ingredients, but to a smaller extent than unbalanced inks.

Regarding the development of oxidized cellulose functionalities, tannic acid (OT-samples) exhibits a remarkable protection against oxidation. Also, during static aging, there is a protection against chain scission. Nevertheless, it cannot be considered for its protective ability in paper conservation as it gives raise to undesired colour changes on paper during aging as observed during mild accelerated aging already.

An important observation is the instant oxidation occurring with inks directly after their application. Especially with unbalanced ink (OU-ink) and unbalanced ink containing copper (OK-ink) this effect is very pronounced, leading to almost three times more carbonyl groups. Most decrease in molecular weight also occurs in this very first period; hence ''weak spots'' within the cellulose backbone undergo instant degradation.

The influence of ink components as well as the extent of oxidation strongly depends on the aging protocol chosen. Temperature seems to play the most important role: when the temperature was still low, even cycling humidity that causes a lot of stress for the model paper will not increase the overall carbonyl group formation to a large extent. At constant humidity aging using higher temperatures the rate of oxidation increases significantly for unbalanced inks within only two further days of aging. This strong increase is not found in balanced ink.

The question arises in how far these model papers will reflect natural occurring ink corrosion on historic papers. In historic papers all kinds of additives, like gelatine, calcium and magnesium compounds, will most probably slow down degradation effects.[27] Nevertheless, both kinds of degradation have been shown to be able to dominate the aging process in metal containing inks or pigments.[28–29] It is not clear yet, which type of accelerated aging will simulate best the typical features of naturally aged paper documents, and further research is needed to clear up this topic.

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