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The effect of the iron-gall ink on permanence in paper by breaking length, degree of polymerisation and thermogravimetric stability of paper during accelerated ageing

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Abstract

Iron-gall inks were the most commonly used writing and very popular drawing media since antiquity. Nowadays, the degradation of this aged paper can be observed. One possible reason for degradation of iron-gall inks is acid hydrolysis of glycosidic bonds. The second one might be iron-catalysed oxidation of cellulose. The aim of this work is to investigate the influence of the iron-gall ink on aged paper. Same behaviour is expected in case of either the breaking length, the thermal stability, the adverse effect on the permanence, or the decrease in temperature of maximal rate of decomposition. These assumptions will be proven or rejected.

Keywords: iron-gall ink, paper degradation, mechanical properties, ageing

Introduction

Paper is a relatively stable material but undergoes ageing process that causes degradation of cellulose. This process relates on presence of acid substances, moisture, oxidative agents or micro-organisms. Especially, deterioration of the paper documents containing the iron-gall inks is supposed to be a combination of two degradation pathways – acid hydrolysis of cellulose and oxidative degradation of cellulose (Ceppan et al. 2006). The iron-gall inks contain transition metals, such as iron or copper, that catalyse the radical oxidation of the substrate, as well as acids, that catalyse theirs hydrolysis (Zou et al. 1994, Neevel 1995). The iron-gall inks are usually made by reaction of iron compound with tannin. The resulting black liquid contains chemical species that can cause degradation (Daniels 2006). According to the most recent findings, a cellulose degradation should be regarded in terms of mixed oxidative and hydrolytic mechanisms (Margutti et al. 2001, Sistach et al. 1998, Strlic and Kolar 2002)

where two reactions are auto catalytically accelerated by active oxygen species and by protons, respectively (Lojewska et al. 2005). One of the main reasons for the corrosivity of iron-gall inks might be presence of the iron ions in the formation of the organic acids or in the electron transfer. The formation of these acids leads to a self-promoting hydrolytic degradation chain reaction or auto-catalysis (Baranski et al. 2004) in the cellulose. The depolymerisation of the cellulose causes the fibre weakness that result in the loss of paper strength and embrittlement during accelerated ageing (Kolar et al. 2006, Kacik et al. 2009). Methods such as viscometry and size-exclusion chromatography, which enable determination of an average molecular weight of cellulose might be used to evaluate the stability of paper. Sufficiently sensitive techniques with the ability to register deterioration at very early stages or at very low levels of changes have been recently developed. According to Daniels (1996), there are two methods to study the oxidation process of the paper under ambient conditions, videlicet: the use of the Russell effect and chemiluminescence. Both methods are based on free radical oxidation of cellulose and they primarily determine the rate of the oxidation. Chemiluminescence showed to be relevant method in polymer degradation studies (Kocar et al. 2004, Rychly et al. 2002, 2004, Strlic et al. 2000, 2001, 2003, Zlatkevich 1989). Other technique such as thermogravimetric analysis judges an impact of these degradation processes on the stability of paper and it is a relevant method in degradation studies, as well (Cardwell and Luner 1976a, 1976b, 1977, Luner 1988, Sun et al. 2004).

In this paper, the degradation processes (the rupture, an adverse effects, etc.) of aged paper are studied in the presence of the iron gall-ink. This degradation is measured and evaluated for different samples using viscosimetry and thermogravimetric technique.

Experimental

Raw material

A commercial, wood-containing newsprint paper (grammage 45 g/m^2, liquor pH: 4.5 – 5.0) with mechanically bleached groundwood (55%), bleached sulphite pulp (20%), scrap fibres (15%), and clay (10%) were used during the following experiments. The samples were 15 cm long and 1.5 cm wide stripes cut, from this paper. Corrosive effect of ink and the role of oxygen was investigated on newsprint paper Charlotte Ahlgren (National Museum, Department of Paper Conservation, Stockholm, Sweden) (Porck 2000).

Model ink systems

Model ink systems were prepared according to Neevel (1995). The molar ratio of transition metal : tannine, was 1.1:2 and the amount of gum arabic was 0.25% in distilled water (w/v). The following chemicals were used: tannic acid (Sigma Aldrich), ferric sulphate heptahydrate (Lachema, Czech Rep..), gum arabic (Sigma Aldrich), distilled water. Water solutions of the inks were applied on the substrate after 15 days of free resting in a dark chamber.

The first batch of the samples (Samples 1) was prepared by drawing of four 1 mm thick lines, next to each other. That results into an one 4 mm wide line. In case of Samples 1a, the lines were drew 7.5 cm from the top edge of the sample, in case of Samples 1b, the lines were randomly drew along the samples. Other batch of samples (Samples 2) was prepared by drawing of one 1 mm thick line randomly along the sample. Next batch (Samples 3) of samples was ink free. These sets of samples were split into aged and unaged samples. The ageing procedure is described below.

Accelerated ageing

Samples of paper were conditioned according to TAPPI T402 om - 93 at 23 ± 1°C, and at relative humidity of air RH = 50 ± 2%, until achieving the homogeneous humidity of test paper, prior the artificial ageing. The samples from all tested deacidification processes were subsequently aged according to STN ISO 5630-4, at 150 ± 2°C. The standard test method for accelerated ageing of paper in which dried ageing was replaced by ageing in a composite bags made of polyethylene/ aluminium/ polypropylene (PET / Al / PE bag). Sets of samples were put into PET/Al/PE bag which was completely sealed, subsequently. This bag was put into another PET/Al/PE bag which was also completely sealed and was once again put into a third (final) sealed PET/Al/PE bag. Finally, samples were in the package of three sealed bags, one in the other. The packages were left in a thermostat for 3 hours at temperature 150 ± 2°C.

Viscosity

For the determination of the degree of polymerisation (DP) of cellulose in paper, the standard viscometric method was used ISO 5351/1. DP was calculated from intrinsic viscosity using the Mark-Houwink.Sakurada equation (Evans 1987): $DP^{0.85} = 1.1 \times [\eta]$. This equation was used to calculate DP for different sorts of paper with varying composition (Strlic et al. 2010). Viscosity, described as degree of polymerisation, was determined on the aged paper with the

iron gall ink (aged Sample 1a) and unaged paper with the iron-gall ink (unaged Sample 1a). The same amount of sample was used in all analysis of intrinsic viscosity. Influence of additives in paper on precision determination can be observed in all analysed samples. Measuring errors are equal within all samples. Therefore, we assume that calculation of DP from intrinsic viscosity using Mark-Houwink-Sakurada equation is possible. Calculation of DP is not strictly necessary as intrinsic viscosity ceould be used for evaluation of the results.

Thermogravimetric analysis

The thermogravimetric analysis of both aged and unaged paper (Sample 1a) with or without presence of the iron-gall ink was carried out on a Mettler TA2 thermoanalyser. The experiments were performed on chunked samples, each weighting 10 mg, heated in sapphire crucibles from 25 °C up to 500 °C at a heating rate 10 °C/min in nitrogen atmosphere (flow 5 l/h).

Breaking length

Breaking length was determined on the aged and unaged Samples 1, Samples 2 and Samples 3 according to TAPPI test Method T494 om – 88. It expresses the loss of fiber strength.

Results and Discussion

Corrosive iron ions and acids in iron-gall inks lead to enhanced degradation of paper, and caused to increase of loss of the degree of polymerization (Csefalvayova et al. 2007, Henniges et al. 2008, Potthast et al. 2008) straightforwardly affects all the mechanical properties (Zervos 2010). Folding endurance is the first strength property to be affected. Stretch at break and tensile energy absorption, together with tearing resistance are less sensitive to degradation than folding endurance, but more sensitive than tensile strength (Bansa and Ishi 1997,1999, Nervos and Moropoulou 2006, Zervos 2007, 2010). It is expected that the amount of applied ink affects ink corrosion. Unaged Samples 3 were ruptured at random positions. The resulting breaking length was in 2025 ± 174 m. Aged Samples 3 had loss of fibre strength 1540 ± 120 m. This proved that the chosen accelerated ageing (3 hours at 150 °C) ensures the loss of fibre strength. In addition, the fibres were more brittle and they lost strength: the loss of 485 m vs. unaged paper. Unaged Sample 1a, paper with the iron gall ink (line width 4 mm) had breaking length 1948 ± 174 m. The average of breaking length measured on aged Samples 1a was 1557

± 195 m. These samples were ruptured in the ink line (Fig. 1.). Difference in breaking length between aged Sample 1a (breaking length 1557 ± 195 m) and aged Sample 3 (breaking length 1540 ± 120 m) was 17 m. The loss of fibre strength was imperceptible. From this, it can be assumed that the iron have not significant detrimental effect on loss of breaking length. Between unaged Sample 1a (breaking length 1948 ± 174 m) and aged Sample 1a (breaking length 1557 ± 195 m) the difference in breaking length was 391 m.

Fig.1. Ruptures of aged Samples 1a

Based on this assumption, the influence of distance between ink line and the edge of the sample was investigated. The Samples 1b were ruptured throughout the drew line. These samples are shown on Fig. 2. In the case of Samples 1b, there was observed loss of fibre strength 1386 ± 218 m. All samples were ruptured in the ink line regardless the distance of the line from the edge of the paper. The results confirmed that iron has a significant detrimental effect on the stability of the paper. The differences between breaking length values of aged paper with iron-gall ink (aged Sample 1a and Sample 1b) at samples with different position of iron-gall ink on the sample are caused by the determination of breaking length. The samples should break in the middle. With the help of these experiments we tried to explain the effect of iron-gall ink on the stability (brittleness) of paper, as shown on Fig. 1 and Fig. 2.

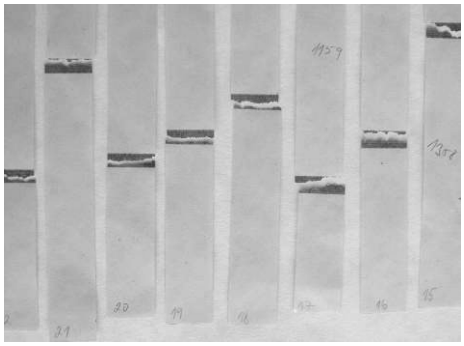

Fig.2. Ruptures of aged Samples 1b

Next, the influence of line width was estimated. The breaking length experiment was evaluated on Samples 2. The results undoubtedly confirmed that the line thickness affected the embrittlement of paper. The loss of fibre strength was 1761 ± 133 m for Samples 2. Also note that in this experiment not every sample, with 1mm thick ink line, ruptured in the line position. Thus, 1 mm wide ink line has no significant effect on the paper permanence. It was observed that during the accelerated ageing, the width of the written line becomes more and more discernable for the brittleness of documents (Kolar et al. 2006). Effect of line width was confirmed. According to Zou et al. (1994) the loss of fibre strength is, in turn, due to depolymerization of the cellulose. It is caused by acid-catalysed hydrolysis and also by catalytic oxidative degradation The hydrolysis rates of polysacharides are higher in acidic media than in neutral and alkaline media (Sundqvist 2004).

During the ageing, a paper samples undergo the degradation process which results into production of low-molecular components. The degradation reactions causes destruction of glycosidic bonds accompanied with the decrease of polymerisation degree. The iron-gall ink has promoting effect on formation of low organic compounds during the ageing process which enhanced degradation within fibre structure (Havermans 1999, Porck and Teygeler 2000). Havermans (1999) reported that the presence of iron-gall ink increases the formation rate of formic acid, acetic acid, and furan derivates as main volatile compounds. The comparison of degree of polymerisation in aged and unaged paper (Sample 1a) with or without ink line is shown on the figure Fig. 3.

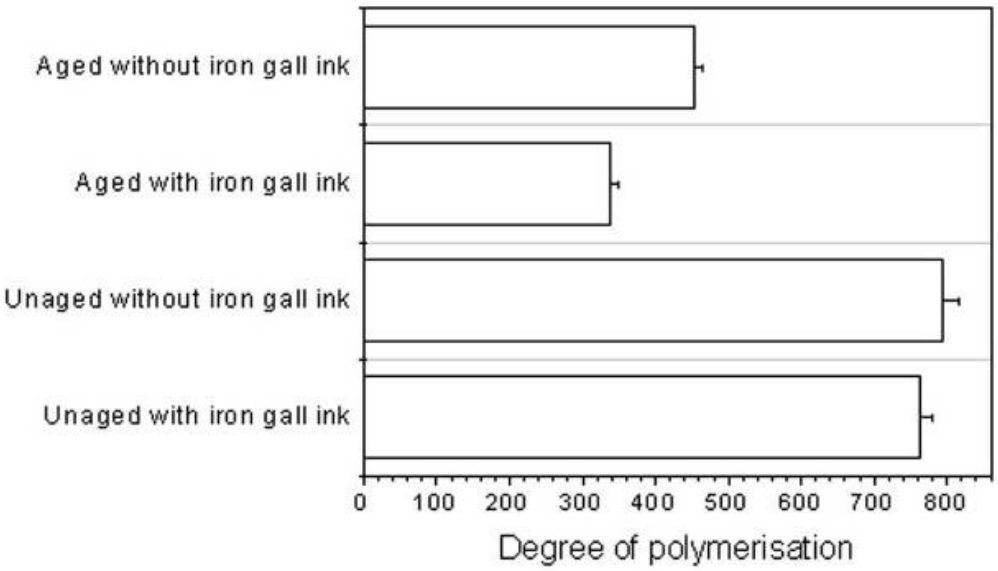

Fig.3. The comparison of degree of polymerisation in aged and unaged paper with or without ink line

It was observed that change in the DP between unaged samples with or without iron-gall ink is subtle (ΔDP 32). An effect of degradation of iron-gall ink in decrease of DP was more obvious during accelerated ageing. DP value of the aged samples without iron-gall ink, was DP=454. In opposite, the DP value for aged samples with iron-gall ink presence was DP=337 Hence, the deleterious effect of iron-gall ink is obvious. The decrease can be expressed by polymerisation degree of 117 units. The drop in the DP of unaged paper without iron-gall ink was about 43 %. In contrary, drop of DP of aged paper containing iron-gall ink was decreased by 56 %. Results demonstrate that iron has a significant detrimental effect on stability of cellulose. This effect was also confirmed by other works (Neevel 1995, Tse et al. 2005, Kolar et al. 2006). Deterioration of the paper, i.e. irreversible chemical and structural changes, is mainly caused by acidic hydrolysis and oxidative agents. Active centres that are involved in acidic hydrolysis contain paper additives (Proniewicz et al. 2001) (for example Al(III) that behaves as Lewis acid). Baranski et al. (2004, 2005) found that acid hydrolysis at highest temperatures and higher Al contents, the Ekenstam equation, does not hold, and consequentially, it can not be regarded as the dominating mode of degradation. There is a proof that acid hydrolysis is the dominating mode of cellulose degradation at lower temperature and lower Al contents. Therefore, on the basis of the research of Baranski et al.

(2004, 2005) it is assumed that the influence of iron on cellulose degradation at higher temperature is the same as in case of aluminium. Mechanisms of degradation are probably mutually interconnected. Dominance of the first or second mechanism dependents on temperature. The effect of ageing on thermal behaviour of unaged and aged paper with or without the iron-gall ink was studied by TG and DTG in the temperature range from 25 °C to 500 °C. The main decomposition takes place in the range 250-400°C with the maximum rate at temperatures which are shown in the Table 1.

Table 1. Thermogravimetric results for unaged and aged samples 1a (accelerated ageing at 150 °C and 3 hours) with or without the iron-gall ink

Samples	**T max**	**Weight loss in the temperature range (%)**		
	(°C)	25 - 200	250-400	Residue500
Unaged paper without the iron-gall ink	354.9	-8.2	-60.2	-74.3
Unaged paper with the iron-gall ink	339.1	-6.4	-47.2	-58.4
Aged paper without the iron-gall ink	339.2	-3.4	-45.1	-57.2
Aged paper with the iron-gall ink	304.1	-4.8	-48.6	-59.1

This implies that the unaged paper had a higher thermal stability than aged papers. These results are in good correspondence with the results published previously. It has been shown that unbleached cellulose tend to had a higher stability than the corresponding degradated cellulosic samples (Sun et al. 2004). The effect of degradation on the lignocellulosic materials was confirmed also in another works (Luner 1988, Sun et al. 2004, Cardwell and Luner 1976a, 1976b, 1977). The measurements showed that the unaged samples have higher stability than aged samples. In addition, the presence of the iron-gall ink, decreased the thermal stability of samples. The decrease is apparent not only at unaged samples but also at aged samples. It concludes that the iron-gall ink lowers thermal stability and decomposition temperature about 35°C. The decomposition temperature was decreased of about 15.7°C in the iron-gall ink free samples. Decrease in decomposition temperature of unaged samples with or without iron-gall ink was 15.8°C. For aged samples decrease was about 35.1°C. This indicates that the thermal stability of the aged paper was decreased by presence of iron-gall

ink. Sun et al. (2004) reported that the thermal stability of the cellulose increases with its purity. Luner (1988) explained that activation energies of artificially aged pulp are consistently lower than those in the control sample. This is a result of carbonyl groups or of reduction in DP as a result of hemicellulose and cellulose hydrolysis.

Conclusion

A degradation process of an aged paper with the presence of the iron-gall ink was benchmarked. It was assumed that the iron will have adverse effect on the cellulose: degree of polymerisation, the thermal instability, or the decrease in temperature of maximal rate of decomposition. It was confirmed that the amount of the iron-gall ink on the paper extents the corrosion process within the paper structure. It has also notable impact on the loss of fibre strength. It was proven that the thermal stability of aged paper substantially decreased against the unaged paper, in the presence of iron-gall ink. Next, the temperature of maximal rate of decomposition was estimated. Similar results were obtained as in preceding tests. There was a notable decrease of this temperature, from 339.1°C to 304.1°C, for unaged paper and for aged paper, both with the iron-gall ink applied. From previous, it can be claimed that the iron-gall ink presented in aged paper has major influence on the performance of this paper.

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