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Investigation of Impact of Stabilization System APTES/KI on Ageing Resistance of Inked Paper

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The investigation of cotton and eucalyptus fibers sheets treated with different historical writing inks has been performed. The inks: Black ink with iron (II) sulphate (**1**, pH 1.52), Black ink with copper (II) sulphate (**2**, pH 2.14); German recipe iron (II) sulphate (**3**, pH 1.62) were used as ink solutions. The paper and the ink treated paper samples were artificially aged (accelerated thermal aging at 80 °C for 90 days) in sealed ampoules and between glass and filter paper. The 3-aminopropyltriethoxysilane (APTES, as deacidification agent) and potassium iodide (KI, as antioxidant) solution in 2-propanol were used as stabilization system for inked paper. The pH measurements and DP data confirm that ageing in sealed ampoules is more destructive to the inked cotton or eucalyptus paper. The results of the experiments indicate that stabilization system APTES/KI have positive effect for not inked paper and during "passive conservation" procedure i. e. between glass plates and filter paper saturated with APTES/KI solution.

Keywords: paper, ageing, deacidification agent, antioxidant, aminosilane.

1. INTRODUCTION

Degradation of historic documents containing metallo-gallate inks is mainly caused by acid hydrolysis and oxidation of cellulose catalyzed by free iron or copper ions. In order to prevent acid hydrolysis the aqueous procedures are often employed in paper conservation. Washing removes water soluble acids from the paper thus increase paper stability [1 – 5]. Removal of acids, acidic degradation products and metal ions may be enhanced at higher temperatures, therefore the treatment of manuscripts with boiling water has been used by conservators for several decades [6 – 7].

Treatment with alkaline solutions removes the impact of acids more effectively thus deacidification and alkalisation of valuable documents leads to better improvement of their longevity. The most common deacidification agents are calcium and magnesium compounds: hydroxides, carbonates, bicarbonates [8 – 11]. However, deacidification treatment does not protect the historical manuscripts against the oxidative decay induced by several transition metals. Conservation procedures of such documents have therefore to include the deacidification of acidic ink ingredients as well as an inactivation of transition metal ions, neutralization of acidity of paper and to provide the document with alkaline reserve to protect it from acids which may accumulate in paper due to air pollutants or internal acid due to the processes of chemical reactions of paper components.

Over the last few decades a number of researches have been performed to confirm the participation of metal ions in the ink corrosion process and to investigate the stabilization of iron gall ink with combined antioxidantand deacidification treatments [12 – 13]. Iodide is known as the inhibitor of cellulose oxidation [14]. Bromine shows the similar. Other inhibitors of oxidation processes, i. e. chelating agents (particularly phytates) are well studied as antioxidants for iron-gall corroded manuscript treatments in paper conservation [15 – 17]. However, phytate treatment is not universal because it must be applied aqueously and does not inhibit the corrosion caused by other transition metal ions present in the inks. Thus phytates may be not effective in stopping ink corrosion since the copper ions are often found in inks either as individual ingredients or as impurities in iron salts. The assorted antioxidant should be efficient in stopping not only iron ions catalytic activity, but other metals ions also.

Conservation treatment has effectively to hinder the paper degradation processes without effect on the information of document. To prevent the undesirable changes caused by water non-aqueous deacidification treatments are only possible for certain documents. The simultaneous paper reinforcement effect is often desirable. In addition, it is important for libraries and archives to treat valuable documents at reasonable cost. Therefore new methods for paper conservation and stabilisation are still being investigated. An interest in nitrogen containing organic compounds in the field of mass deacidification of books has recently risen [18 – 20]. It is noticed that paper treated with aminoalkoxysilanes shows a significant improvement of mechanical properties besides of increased pH. Supposedly such improvement can arise due to hydrolysis and self-condensation of the treatment agent and the network formation within the cellulose fibres [19 – 21].

The aim of our study was to investigate the effect of 3-aminopropyltriethoxysilane (APTES) as the deacidification agent together with KI as an antioxidant on the ageing stability of inked paper. The different ageing procedures, i. e. in sealed ampoules and between glass plates were used.

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2. EXPERIMENTAL

Two types of paper (70 g/m^2) were manufactured for an experiment: paper consisting of pure cellulose fibres (cotton; C) and paper of bleached sulphate hardwood pulp (eucalyptus; E). Paper sheet samples in appropriate size of A3 format were made on leaf-casting equipment, developed in 1985 by Per M. Laursen, a Dutch paper conservator [22]. After casting all papers were placed for pressing between sheets of non-woven synthetic material and filter paper. The moistened filter paper was replaced several times until the paper samples became dry. The dried samples were pressed in the screw-press between the sheets of filter paper for 10 days.

The paper samples were evenly inked using three different writing ink samples prepared by the following recipes [23]. Analytical grade (Aldrich or Fluka) reagents were used for the preparation of inks:

(**1**) Black ink with iron (II) sulphate; 66.8 ml of distilled water was mixed with 7.688 g of powdered oak galls and the mixture was stored for 4 days. To this mixture 2.528 g of iron (II) sulphate ($FeSO_4 \cdot 7H_2O$;), 0.2 g of sodium chloride (NaCl), 2 ml of 10 % acetic acid and 0.318 g of alum ($KAl(SO_4)_2 \cdot 12H_2O$) were added. The obtained mixture was stored for 2 weeks with intermediate mixing and filtered (pH 1.52)

(2) Black ink with copper (II) sulphate; 66.8 ml of distilled water was mixed with 7.688 g of powdered oak galls and the mixture was stored for 4 days. To this mixture 2.528 g of copper (II) sulphate ($CuSO_4 \cdot 5H_2O$), 0.2 g of sodium chloride (NaCl), 2 ml of 10 % acetic acid and 0.318 g of alum ($KAl(SO_4)_2 \cdot 12H_2O$) were added. The obtained mixture was stored for 2 weeks with intermediate mixing and filtered (pH 2.14)

(3) German recipe: 100 ml of distilled water, 0.7 ml of 10 % hydrochloric acid (HCl;), 0.77 g of gallic acid ($(HO)_3C_6H_2COOH$), 1.0 g of gum arabicum, 2.34 g of tannin (Kremer Pigmente), 0.1 g of phenol (C_6H_5OH;) and 3.0 g of iron (II) sulphate ($FeSO_4 \cdot 7H_2O$) were carefully mixed (pH 1.62).

For this study the sheets of paper from cotton and eucalyptus cellulose were saturated with ink **1**, **2** and **3**. Another set of sheets were immersed into the same inks with subsequent saturation with APTES solution in 2-propanol (conc. 9.1 % in weight) and KI solution (1 g in 3 ml $H_2O$and 97 ml 2-propanol). The treated sheets of paper were subjected to ageing in different ways. The samples of one set (inked only and inked with subsequent saturation by APTES/KI) were sealed in glass ampoules and aged in oven at 80 °C for 90 days. The samples of the other set were interleaved by pure filter paper. For the last set of samples the interleaving was done with filter paper saturated by APTES/KI. The interleaved samples were impacted between two glass plates to simulate the libraries conditions where the leaves of books or other documents are hold tight in shelves. The interleaved samples were aged in an oven at 80 °C for 90 days.

The cold-water extraction method was used for the pH measurements. The surface pH of the paper was determined by using InLab 423 electrode. The small amount of samples (0.002 g) was suspended in distilled water. The pH meter Mettler-Toledo MP220 was employed for measuring pH values of suspended samples. ISO standard 5351/04 was followed for viscosity determination and for the estimation of degree of polymerization (DP). The glass viscometer 1C 48 Ubbelholde (capillary 0.86 mm) and cupric ethylenediamine (CED) as solvent were used for the measurements. The error values of the measurements were about ±1.5 %.

The notations for the treatments and the paper samples are as follows:

C – pure cotton paper; E – paper from eucalyptus cellulose.

1C, 2C, 3C – cotton paper saturated with ink 1, 2 and 3 respectively; 1E, 2E, 3E – eucalyptus paper saturated with ink 1, 2 and 3 respectively.

C + A/KI – cotton paper saturated with APTES/KI; 1C + A/KI – cotton paper saturated with ink 1 with subsequent immersion in APTES/KI; 2C + A/KI – cotton paper saturated with ink 2 with subsequent immersion in APTES/KI; 3C + A/KI – cotton paper saturated with ink 3 with subsequent immersion in APTES/KI.

E + A/KI – eucalyptus paper saturated with APTES/KI; 1E + A/KI – eucalyptus paper saturated with ink 1 with subsequent immersion in APTES/KI; 2E + A/KI – eucalyptus paper saturated with ink 2 with subsequent immersion in APTES/KI; 3E + A/KI – eucalyptus paper saturated with ink 3 with subsequent immersion in APTES/KI.

3. RESULTS AND DISCUSSION

Since the cellulose degradation products formed during ageing influence the pH and consumption of the alkaline reserve, the pH measurements of aged samples were performed. The ageing of paper in sealed ampoules as well as between glass plates were performed at 80 °C for 90 days. The comparison of pH values of cotton and eucalyptus paper samples after ageing in sealed ampoules with these interleaved and aged between glass plates has shown that the ageing results may be influenced by ambient atmosphere (Fig. 1).

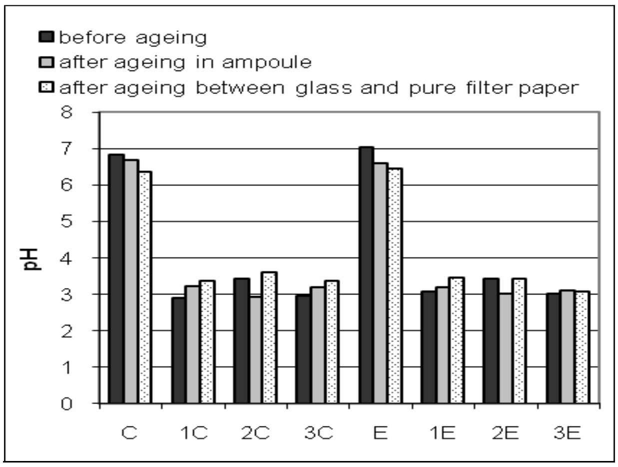

Fig. 1. The impact of ageing atmosphere on the pH values of inked and virgin paper (at 80 °C for 90 days)

The pH values of inked samples were found to be higher after ageing between glass plates as compared with pH of the samples aged in sealed ampoules. The pure cotton and eucalyptus paper samples showed inverted results. Supposedly the inked paper emits more volatile compounds during ageing which in case of the sealed ampoules were not removed from the samples environment and thus contributed to paper degradation. The results of pH determination indicated that ageing in the sealed ampoules was more destructive with respect of the inked paper.

To evaluate the effect of APTES/KI system on the stability of inked paper the pH measurements of aged samples were performed. For a comparison the pH of new paper samples (inked and uninked) were determined as well. The results are given in Figure 2 and Figure 3.

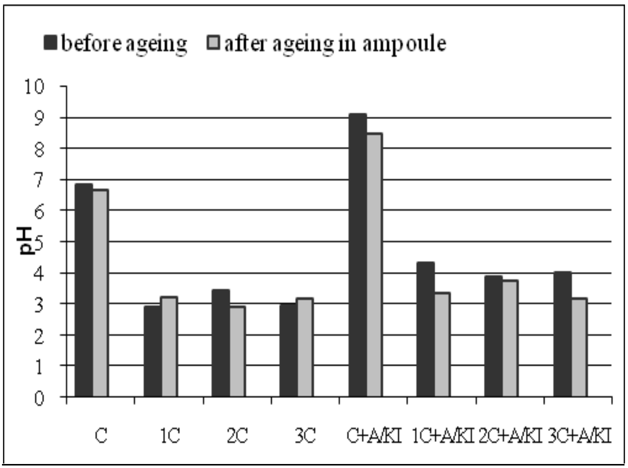

Fig. 2. The pH values of untreated and APTES/KI treated cotton paper before and after ageing at 80 °C for 90 days in sealed ampoules

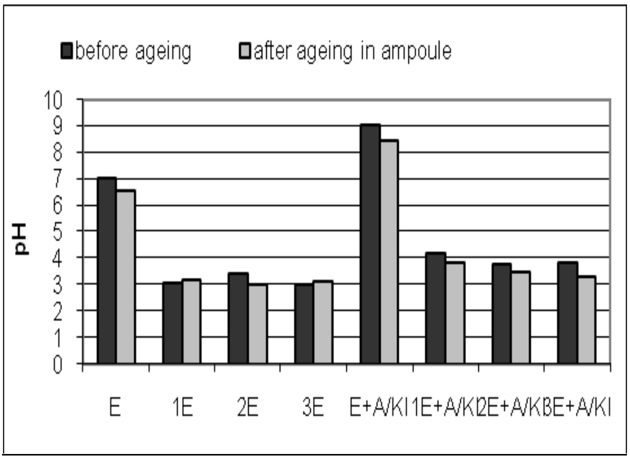

Fig. 3. The pH values of untreated and APTES/KI treated eucalyptus paper before and after ageing at 80 °C for 90 days in sealed ampoules

The comparison of acidity of untreated and treated with APTES/KI paper samples (inked and uninked cotton and eucalyptus paper) before and after ageing showed that the pH values decreased after ageing in all cases, but APTES/KI treated samples showed higher pH after ageing as compared with untreated samples (Figs. 2, 3).

The ageing results of interleaved paper samples indicated that the stabilisation system might be effective when used in the manner of "passive conservation". All the samples (inked and uninked) aged between APTES/KI treated filter paper show higher pH after ageing as compared with those aged between pure filter paper (Fig. 4).

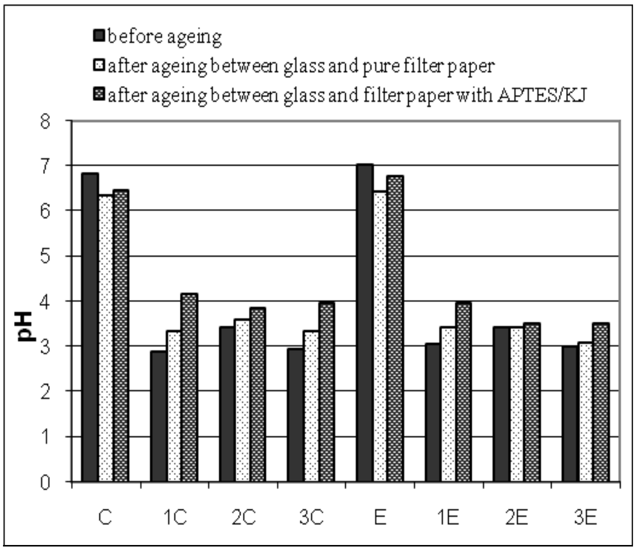

Fig. 4. The impact of quality of interleaving paper on the pH values of interleaved inked and uninked cotton and eucalyptus paper aged at 80 °C for 90 days between the glass plates

The method most commonly used in the literature for the characterization of cellulose degradation involves the determination of either the Chain Scission Number (CSN) or the Scission Fraction of Cellulose Unit (SFCU) as a function of degree of polymerisation (DP) [24]. DP can be determined from the measured change of viscosity of paper solutions. Viscometric determination of DP was performed according using standard procedure, using fresh cupriethylenediamine as solvent. DP was calculated from the intrinsic viscosity number $[\eta]$ using the Immergut equation ($[\eta] = Q\mathrm{DP}^{\alpha}$, where Q = 1.33 ml/g and α=0.905) [25].

The DP data of cotton and eucalyptus non-inked and inked samples before and after ageing in sealed ampoules and between pure filter paper and glass plates are shown in Figure 5.

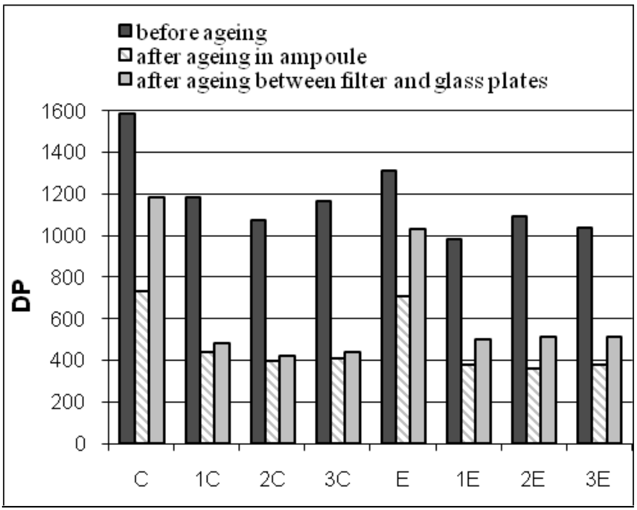

Fig.5. DP values of cotton and eucalyptus paper and inked samples after ageing in sealed ampoule and between filter paper and glass plates (before and after ageing at 80°C for 90 days)

The significant decrease of DP was observed for cotton (54 %) and eucalyptus (46 %) paper after ageing in sealed ampoules, while the less decrease of DP was observed for cotton (27 %) and eucalyptus (18 %) paper after ageing between glass plates was obtained. The immersing of paper into ink (1–3) solutions caused decrease of DP as compared with pure cotton 1585 or eucalyptus 1320 paper. The lowest DP values were obtained after ageing in sealed ampoules. The polymerization degree data confirm, that during the ageing procedure in sealed ampoules produce more "aggressive" medium, than between the glass plates.

The well know antioxidant – potassium iodide is thought to act as catalytic peroxide decomposer, and is thus capable of interfering with the oxidizing agent irrespective of the transition metal. In the second experiment the paper samples were treated with solution of antioxidant KI and deacidification agent 3-aminopropyltriehoxysilane. The values of DP of paper and inked samples after ageing in ampoules or between glass plates are given in Fig. 6 and Fig. 7.

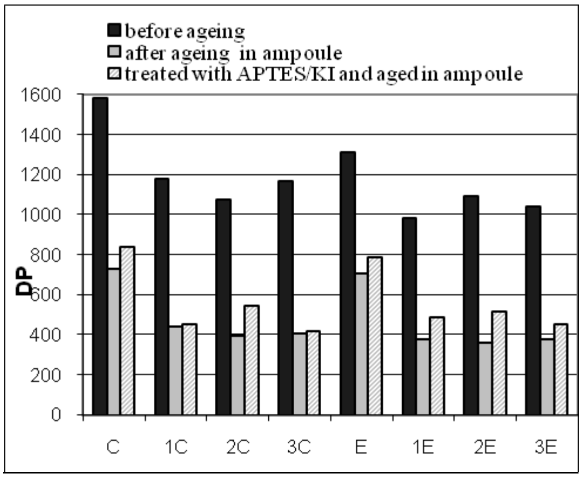

Fig. 6. DP values of cotton, eucalyptus paper or inked samples and treated with APTES/KI solutions in sealed ampoules (before or after ageing at 80 °C for 90 days)

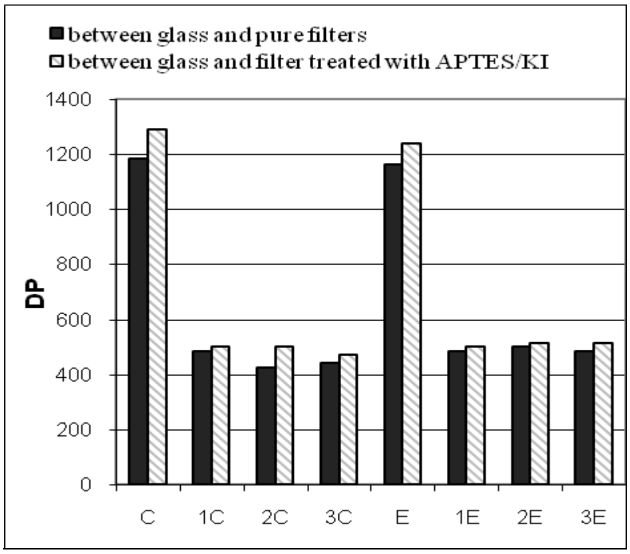

Fig. 7. The DP values of paper cotton and eucalyptus samples aged between glass and pure filters paper or between glass and filters paper treated with APTES/KI solution; all samples were aged at 80 °C for 90 days

The results presented in Fig. 6 and Fig. 7 demonstrate that the most positive impact of APTES/KI solution is for 2 ink corrosion, which contain copper (II) sulphate. Also, stabilisation solution APTES/KI is capable of inhibiting degradation of uninked paper after ageing between glass and filter paper treated with APTES/KI solution. The difference of "positive behaviour" of stabilisation system APTES/KI for uninked and inked paper samples can be explained by difference of pH values of the paper samples. The pH values of cotton and eucalyptus paper after treatment with APTES/KI solution were high (about 8.5 – 9), while pH of the inked samples were still low (about 3.5 – 4.5). Thus, the experiment also indicated that it is necessary to add more deacidification agent for obtaining alkali medium for improving stabilisation system and obtaining major positive effect.

CONCLUSIONS

The different ageing procedures for inked and uninked cotton and eucalyptus paper samples in sealed ampoules and between glass plates at 80 °C for 90 days were tested. The pH measurements and DP data confirm that ageing in sealed ampoules is more destructive with respect of the inked cotton or eucalyptus paper. The results of the experiments indicate that stabilisation system APTES/KI has a positive effect for not inked cotton and eucalyptus paper in "passive conservation" procedure i. e. between glass plates and filter paper saturated with APTES/KI. However, the experiment also indicated that it is necessary to add more deacidification agent for obtaining alkali medium and the improving stabilisation system.

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