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Investigation of the impact of organic and inorganic halides on the ageing stability of paper with iron gall ink

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Degradation of cellulose in historic manuscripts with iron gall ink leads our heritage to deterioration. Direct aqueous or non-aqueous methods of treatment, which are often used in practice, can damage the authenticity of documents. Therefore, other methods without any wet curative procedures during treatment are in great request.

The aim of this work was to evaluate the efficiency of interleaving treatments performed with interleaves containing organic (tetrabuthylammonium bromide and 1-ethyl-3-methylimidazolium bromide) and inorganic (KI and KBr) halide salts on the stability of paper with iron gall ink during ageing. The effect of interleaving was compared with 1) the efficiency of direct treatment of samples and 2) the established conservation procedure – calcium phytate/calcium hydrocarbonate treatment.

To evaluate the stabilization effect of different compounds and the efficiency of particular conservation technique measurements of the polymerization degree (viscosimetry, size exclusion chromatography – SEC) and pH were performed before and after accelerated ageing. Colour change in paper samples was determined by reflection measurement using an integrating sphere with a halogen light source. The condition of paper fibers was studied using optical microscopy and scanning electron microscopy (SEM).

The tentative results demonstrate that the effective stabilization of paper containing iron gall ink during ageing may successfully be achieved by interleaving using alkaline paper impregnated with KBr.

Keywords: paper, iron gall ink, ageing, stabilization, antioxidants, degradation, deacidification

INTRODUCTION

Historical documents containing iron gall ink from different periods of time constitute a big part of written heritage. Unfortunately, the main constituents of iron gall inks – acids and the excess of transition metal compounds – can cause degradation processes of paper destroying it by acidic hydrolysis and the oxidative breakdown of cellulose through Fenton's reaction.

Oxidative degradation of paper may be retarded by the treatment of various antioxidants, such as calcium phytate, some quaternary ammonium salts or imidazolium-based ionic liquids. The most prevalent technique to prevent iron gall ink corrosion is the so-called "calcium phytate–calcium hydrocarbonate treatment method" [1]. Calcium phytate belongs to the group of chelating agents and has a strong stabilizing effect of forming chelate complexes with metal ions thus blocking its further negative influence to the paper [2]. However, an usual stabilization procedure involves the immersion of documents in an aqueous solution

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of calcium phytate and the deacidification with a calcium hydrocarbonate solution [3]. Since water-based solutions can cause negative side effects to the documents, such as a drastic modification of the paper/ink composition, mechanical stress of damaged papers, substantial changes in colour and document appearance, non-aqueous methods of treatment were investigated [2].

For the last twenty years, some quaternary ammonium salts (tetrabutylammonium bromide (TBABr)) and imidazolium-based ionic liquids (1-ethyl-3-methylimidazolium bromide (ImBr)) are known as organic antioxidants which decompose hydrogen peroxide [4, 5]. These organic antioxidants are soluble not only in water, but in less polar solvents like ethanol. They are non-volatile, have a low impact on the environment and human health, thus recognized as compounds for green chemistry [6]. These antioxidants interfere with the free radical oxidation by eliminating reactive agents. According to different chemical actions, the antioxidants may be divided into 1) free radical scavengers, which remove primary peroxy radicals and 2) antioxidants, which convert hydroperoxides to their corresponding alcohols [7, 8]. However, an organic halide based treatment is implemented after a conventional aqueous deacidification procedure, meaning that the global method of treatment remains water-based with related side effects [9]. Thus, the choice of secure conservation methods is still limited.

Recently, new stabilization techniques avoiding any wet curative procedures were proposed. Dry stabilization techniques (indirect treatments) consist of placing a document in contact with interleaves – sheets of paper impregnated by active compounds. Interleaves can be charged with an alkaline buffer and other organic or inorganic antioxidants which can migrate from interleaves to the document as well as acids or/and metal ions from the document to the interleaves, thus achieving the paper stabilization and avoiding major negative side effects [10–12].

The aim of this study was to evaluate the efficiency of interleaving treatments performed with interleaves containing organic or inorganic halide salts intended to retard the ageing of paper with iron gall ink and to compare with the efficiency of the direct treatment of samples with non-aqueous organic halide solutions and with the established aqueous conservation procedure – calcium phytate and deacidification with calcium hydrocarbonate.

EXPERIMENTAL

Preparation of ink and inked samples

Model iron gall ink was prepared according to the following recipe: 2.34 g of tannin and 0.77 g of gallic acid monohydrate were mixed with 100 ml of distilled water. After mixing, 3 g of iron(II) sulphate heptahydrate and 0.7 g of 10% solution of hydrochloric acid were added. The obtained mixture was stored for 5 days periodically stirring it [13].

Sheets of the filter paper Whatman® (6.5 × 9.0 cm) made of pure cellulose were prepared. One part of sheets were evenly inked (immersion lasted for 10 s) using a made-up writing ink (filtered and diluted with distilled water 1:2) and allowed to dry at room temperature (Fig. 1a).

The second part of the filter paper sheets was dashed using a pen (to simulate the manuscript situation) and left to dry at room temperature (Fig. 1b). The third part of the samples (with iron(II) sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$)) was prepared by following these steps: the sheets of filter paper were immersed into a 0.01% solution of $FeSO_4 \cdot 7H_2O$, kept there for 2 h and allowed to dry at room temperature. The dashed paper samples and those with iron(II) sulphate heptahydrate were used to estimate the degree of colour change in the treated and not treated paper after artificial ageing.

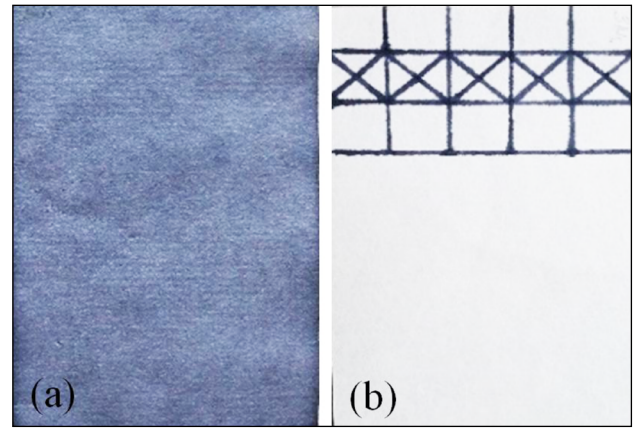

Fig. 1. Filter paper sheet inked with iron gall ink (a); filter paper sheet dashed with iron gall ink (b)

Preparation of the samples for artificial ageing

The inked paper samples were stabilized by two different types of treatments: direct and indirect treatment (Table 1). The direct treatment consisted of the immersion of the inked paper samples in aqueous or non-aqueous active stabilization solutions of an alkaline buffer and organic antioxidants. The inked paper samples were treated by a 0.6% solution of 1-ethyl-3-methylimmidazolium bromide (ImBr) and a 1% solution of tetrabutylammonium bromide (TBABr) in ethanol. The indirect treatment consisted in placing the inked paper samples in contact with the interleaving filter paper impregnated with different types of active solutions and the alkaline buffer: the samples were placed between the interleaves impregnated with a 1.2% solution of ImBr, a 2% solution of TBABr, 2% solutions of KI and KBr (indirectly treated samples marked as □). The filter paper Whatman® made of pure cellulose was used for interleaving. The interleaves (leaves 6.5 × 9.0 cm) and the inked paper samples were soaked in different concentration solutions of halide salts for 10 min and allowed to dry at room temperature.

Table 1. **Notations and description of samples**

Notations	Description
IP_C	Inked paper (control; not for ageing)
IP	Inked paper
IP+Ca	Inked paper directly treated by solution of $Ca(HCO_3)_2$
IP+ImBr	Inked paper directly treated by solution of ImBr
IP+TBABr	Inked paper directly treated by solution of TBABr
IP+TBABr+Ca	Inked paper directly treated by solutions of $Ca(HCO_3)_2$ and TBABr
IP+ImBr+Ca	Inked paper directly treated by solutions of $Ca(HCO_3)_2$ and ImBr
IP+Phyt+Ca	Inked paper directly treated by solutions of calcium phytate and $Ca(HCO_3)_2$
IP□P	Inked paper impacted between interleaves of pure filter paper
IP□Ca	Inked paper indirectly treated by impacting between interleaves containing $CaCO_3$
IP□TBABr+Ca	Inked paper indirectly treated by impacting between interleaves containing TBABr and $CaCO_3$
IP□ImBr+Ca	Inked paper indirectly treated by impacting between interleaves containing ImBr and $CaCO_3$
IP□KI+Ca	Inked paper indirectly treated by impacting between interleaves containing KI and $CaCO_3$
IP□KBr+Ca	Inked paper indirectly treated by impacting between interleaves containing KBr and $CaCO_3$
Treatments of the filter paper samples dashed with iron gall ink (IP') same as these immersed in iron(II) sulphate heptahydrate solution (PFe) are marked analogically.	

Table 2. **ΔE value perception scale**

Delta E	Perception
0–1	Not perceptible by human eyes
1–2	Perceptible through close observation
2–10	Perceptible at a glance
11–49	Colours are more similar than opposite
100	Colours are exactly opposite

Calcium carbonate ($CaCO_3$) was introduced as an alkaline buffer in some samples using a saturated solution of calcium hydrogen carbonate – $Ca(HCO_3)_2$. Each immersion in this solution lasted for 15 min. Then the samples were dried at room temperature.

Artificial ageing

Two sets of samples were prepared and aged. The indirect treatment and ageing of inked paper samples were performed as depicted in Fig. 2: an inked paper sample was impacted between the impregnated interleaves and two glass plates and aged. The directly treated inked paper samples were aged separately (no contact with interleaves or glass plates).

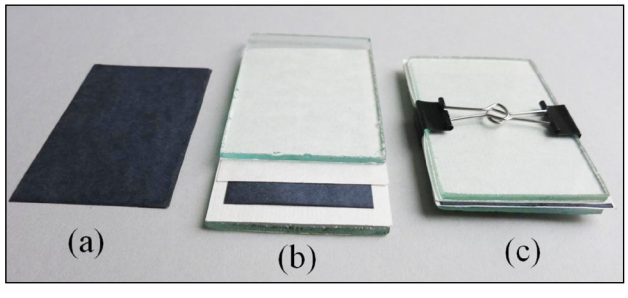

Fig. 2. The inked paper sample (a); the sample interleaved with filter paper (b); the sample interleaved and impacted between two glass plates (c)

Thermal accelerated ageing for all samples was performed in an oven in a humid environment at 70 ± 2 °C and 80% RH for 430 h. Two sets of directly treated samples (set I, set II) and two sets of indirectly treated samples (set I, set II) were aged.

Methods of analysis

To evaluate the stabilization effect of different compounds and the efficiency of particular conservation technique the measurements of polymerization degree – DP (viscosimetry, size exclusion chromatography – SEC) and pH determinations were performed before and after accelerated ageing. The colour change of the paper samples was determined by reflection measurement using an integrating sphere with a halogen light source. The condition of paper fibers was studied by SEM and optical microscopy.

Determination of polymerization degree

Viscosity measurements of the cellulose solution of the samples in 0.5 M cupriethylenediamine (CED) were carried out with a capillary viscometer (type 53013, K – 0.03, Cat. No. 9.268313) according to the ISO 5351/04 standard [14] in the following way: the samples were cut into little pieces and soaked with few pieces of a copper wire in a flask with 25 cm^3 of distilled water. The paper suspension was then dissolved in a 25 cm^3 of 0.5 M CED solution, blown through with nitrogen gas for several minutes and stirred for additional 5 min. For each sample two CED solutions were

prepared and for each solution the measurement was repeated five times. The average value of DP was calculated according to the formula

$$[\eta] = K[DP]^{\alpha},$$

where [η] is the limiting viscosity number; K is the constant equal to 1.33 ml/g; DP is the degree of polymerization; α is the coefficient of cellulose in CED solution which is equal to 0.905 [15].

SEC measurements

The original samples were derivatized using phenyl isocyanate to obtain cellulose tricarbanilate (CTC) which were dissolved in tetrahydrofuran (THF) prior to each SEC analysis. The derivative was prepared in the following way [15]:

- 20 mg of the sample cut into little pieces was placed in a glass vial and dried at 105 °C temperature for 0.5 h.
- The pre-dried sample was treated with 1 cm^3 of water-free pyridine and 0.1 cm^3 of phenyl isocyanate (PIC), several small glass balls were dropped into a glass vial, sealed, and maintained at 80 °C for 48 h.
- To terminate the substitution reaction 1 cm^3 of methanol was added and the reaction mixture was then cooled to room temperature.

To minimize the possibility of rough random errors each sample was analyzed twice. Prior to the SEC analysis, the CTC solutions were diluted 1:10 with THF and filtered using 0.45 μm PTEE syringe filters (OlimPEAK).

The molar masses presented in this paper refer to the cellulose after calculations of the substitution degree in CTC, which was assumed to be 2.925 [16].

The DP of the reference and aged samples was calculated from the ratio

$$DP_w = \frac{M_w}{M_{mono}},$$

where M_{mono} is equal to the molar mass of a substituted monomer unit of cellulose and has a value of 510 [16].

The average molecular mass and molecular mass distribution were determined using a Viscotek GPSmax chromatographic system which consists of a Viscotek TDA305 (Viscotek Triple Detector Array) incorporated with a refractive index, light scattering and viscosity detectors. Separation of the CTC samples was performed with the use of a set of two TSK-GEL GMHhr-M polystyrene-divinylbenzene columns which were termostated at 30 °C. THF was used as an eluent with a flow rate of 0.5 cm^3/min.

pH measurements

An additional parameter to study was the pH measurements performed before and after the accelerated ageing. The pH measurements were performed using a cold extraction according to the ISO standard 6588-1:2005 [17].

For cold extraction approximately 0.02 g of the sample was left to swell in 1 cm^3 of demineralized water for one hour and then extracted. Two extracts of each sample were prepared and measurements were performed at room temperature.

Colour change measurements

The colour change of the paper samples before and after the particular treatment and accelerating ageing was recorded by reflection measurement using an "Avantes" integrating sphere with a halogen light source. Based on the spectral power distribution in CIE 1931 xy chromaticity distortion vectors the space ΔE was calculated. The results were compared with the ΔE colour perception scale range from 0 to 100 [18–20].

Observation of paper fibers condition

Cellulosic fibers – the main constituent of paper – tend to lose their flexibility and friability during ageing processes. The structural changes of paper and the condition of cellulosic fibers were studied by HITACHI TM 3000 scanning electron microscopy coupled with light element energy dispersive X-ray microanalysis (SEC-EDX) under the 15 kV charge-up reduction mode. Photographic images of the edge of broken samples were taken by a MD 750 & KOEHLER Leica optical microscope under 4 × magnification.

RESULTS AND DISCUSSION

Evaluation of degradation of cellulose

The results show that the process of degradation of all antioxidant-treated and deacidified samples was slower and depends on the used antioxidant. Moreover, in order to achieve the best stabilization effect an alkaline buffer is necessary (Fig. 3). The degree of polymerization (DP) of the inked, untreated and aged paper sample (IP) decreased by ~56–62% compared with that of the inked, untreated but not aged paper sample (IP_c), while the DP of the inked and treated with the $Ca(HCO_3)_2$ paper sample after ageing decreased by ~30–36% compared with that of IP_c. Moreover, the results of comparing antioxidant-treated, alkalized and aged inked paper samples (IP+ImBr+Ca; IP+TBABr+Ca) with the just antioxidant-treated aged inked paper samples (IP+ImBr; IP+TBABr) show that the DP of the IP+ImBr+Ca and IP+TBABr+Ca samples decreased by ~23–29% while the DP of the IP+ImBr and IP+TBABr paper samples decreased by ~42–56%. Therefore, due to the focus of this study, there will be no further analysis of samples, which did not attain deacidification.

According to the presented results, the direct aqueous treatment with Ca-phytate and deacidification with $Ca(HCO_3)_2$ of the samples had the greatest positive impact on the stabilization of paper. DP of the IP+Phyt+Ca sample decreased by ~12–26% after ageing. Also, the results of

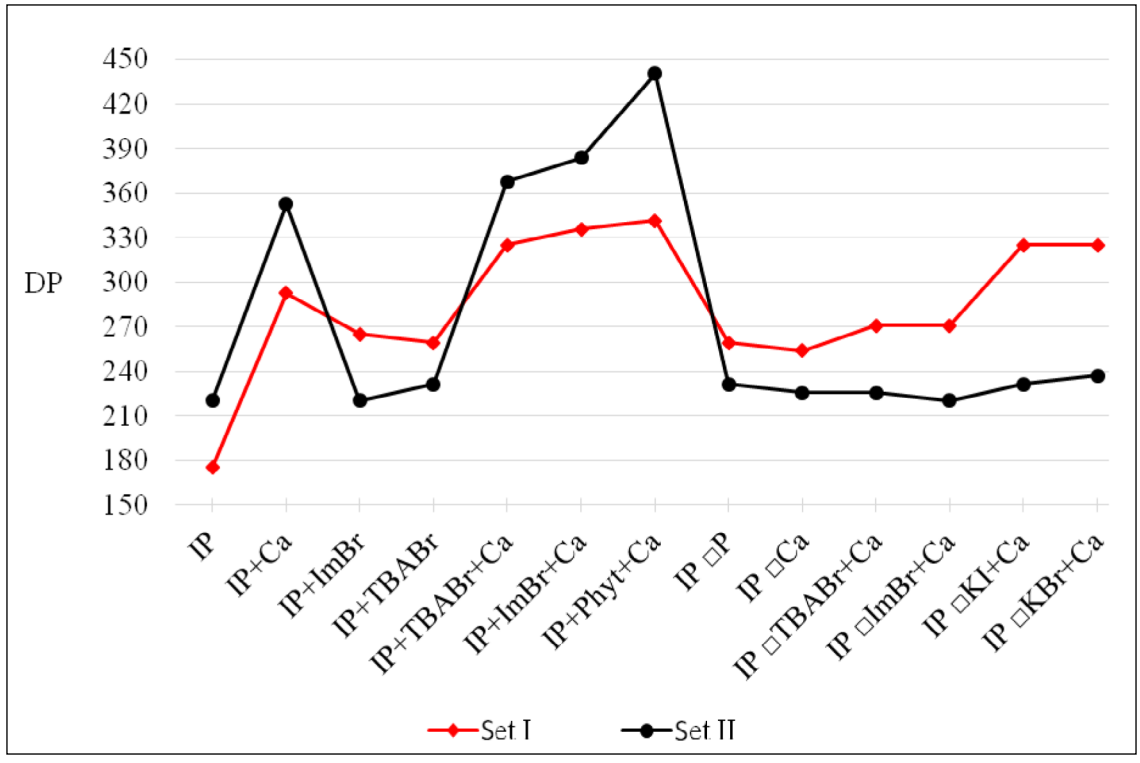

Fig. 3. Average polymerization degree of cellulose (viscosimetry data) of differently treated and aged IP samples

the direct treatment by non-aqueous TBABr and ImBr and aqueous $Ca(HCO_3)_2$ showed that DP decreased by ~23–29% compared with IP_c (Fig. 4). However, the interleaves charged with the same TBABr and ImBr organic halide salts used for the indirect treatment had not shown a good stabilization effect. DP of IP□TBABr+Ca and IP□ImBr+Ca decreased by ~41–56% (Fig. 5).

Applying the indirect treatment on paper with iron gall ink the best results were achieved by ageing the inked paper samples between the interleaves charged with inorganic halide

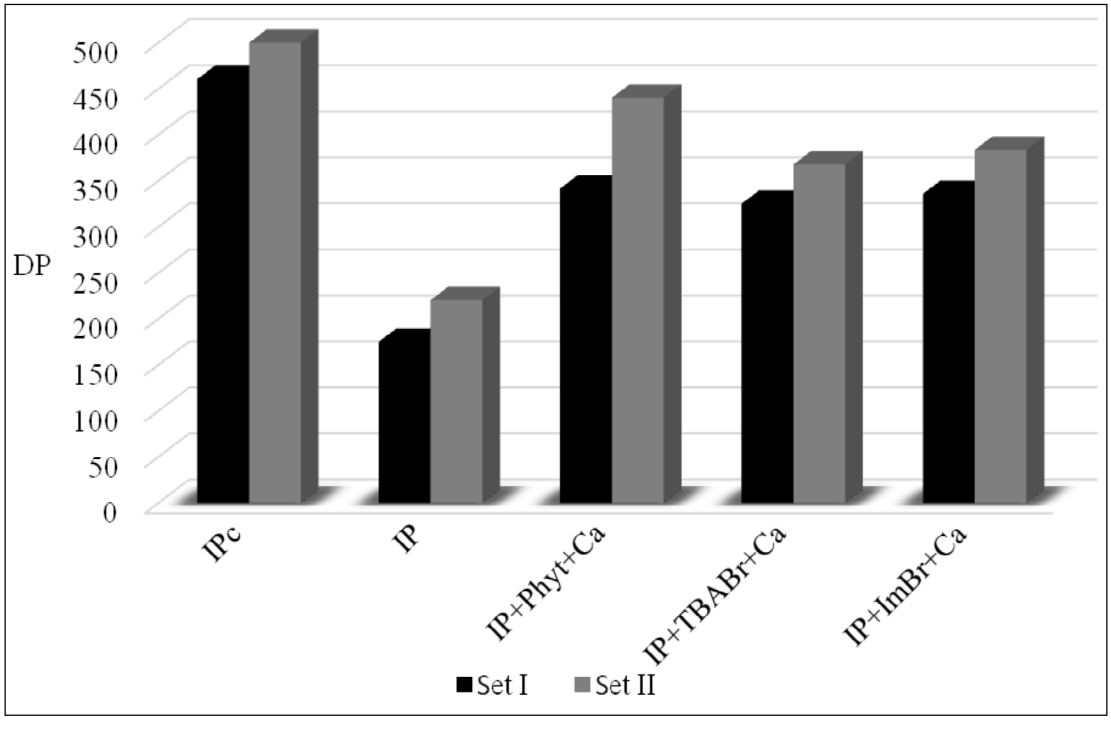

Fig. 4. Average polymerization degree of cellulose (viscosimetry data) of inked paper control and differently treated and aged IP samples

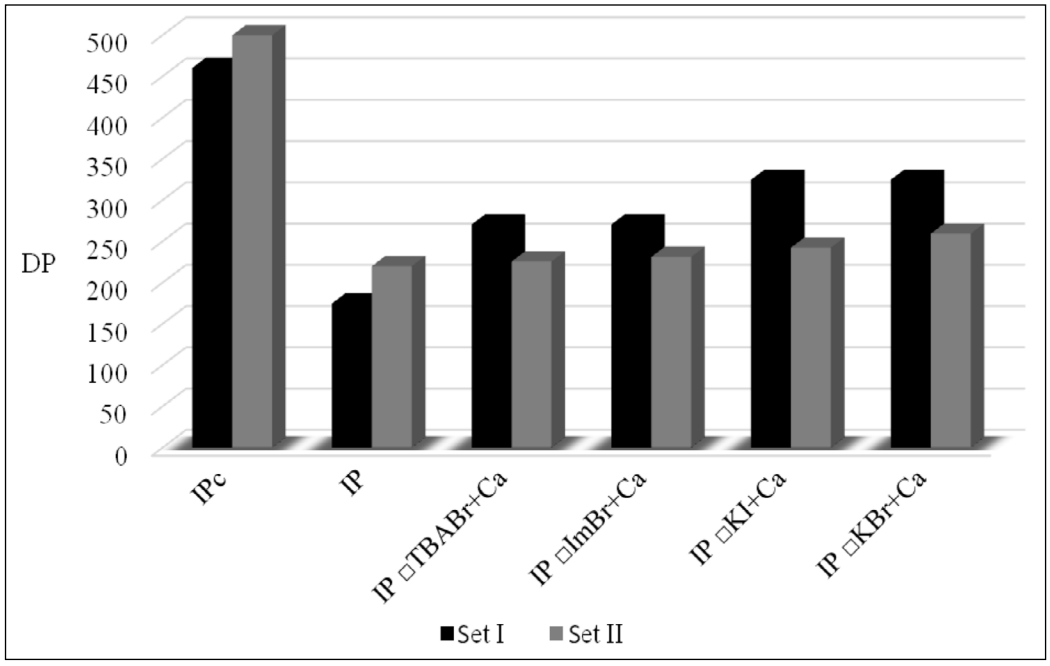

Fig. 5. Average polymerization degree of cellulose of IP samples (viscosimetry data) aged between differently treated interleaves

salts KI or KBr together with $CaCO_3$ (Fig. 5). According to the results, DP decreased by ~29–54% compared with IP_c.

The stabilization effect of the inked paper samples aged between the interleaves charged with organic or inorganic halide salts and the alkaline buffer could differ possibly because of various mobility of molecules: KI and KBr can easily migrate from the interleaves to the samples while migration of TBABr and ImBr from the interleaves to the samples is complicated because of bigger molecules.

Results of viscosity vs results of SEC

To evaluate the stabilization effect of different antioxidants on model paper with iron gall ink, the method based on size exclusion chromatography (SEC) of the cellulose samples derivated using phenyl isocyanate was used. The method enables determination of the average molar masses of the sample because of a small mass required for the analysis and this determination method is more accurate. The results obtained by SEC analysis were compared with the results gained by viscosimetry (Fig. 6).

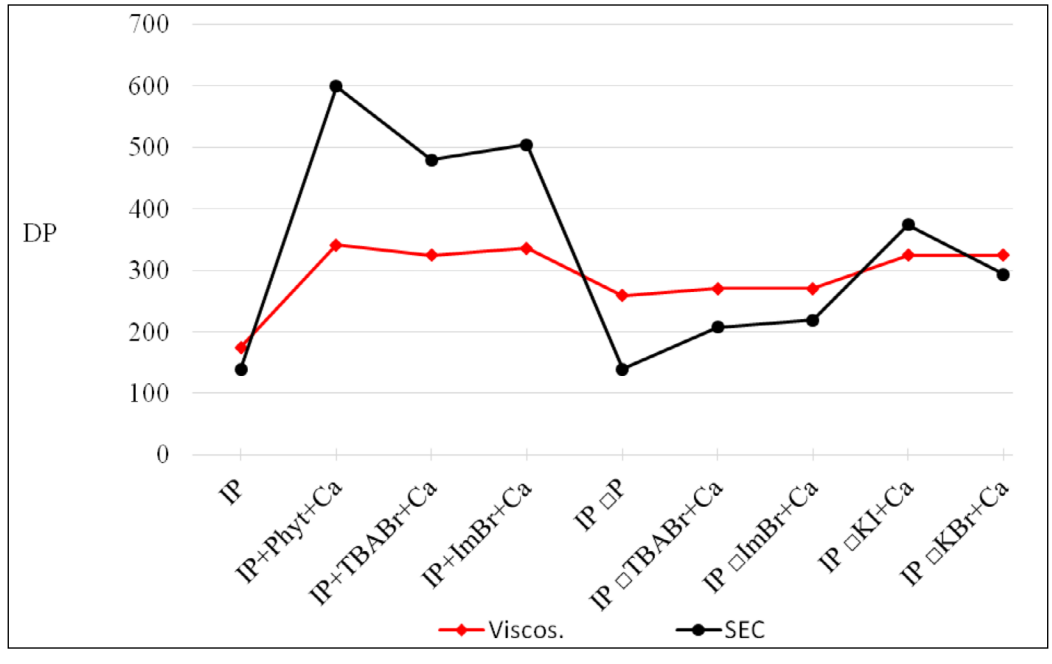

Fig. 6. A comparison of the average polymerization degree of cellulose of aged IP samples obtained by two methods – viscosimetry and SEC

The values of the degree of polymerization (DP) determined by SEC and those obtained by viscosity measurements are slightly different. However, it is obvious that the stabilization effect of dissimilar treatments and different halide salts for paper samples show the same tendency.

Evaluation of cellulosic fiber condition

The visual structural changes of the model paper samples were evaluated by interrupting a paper sample strip and shooting its rupture area with an optical microscope, while a paper cross-section was analysed by SEM.

The images of the rupture area of samples can demonstrate the suitability of appropriate treatment for paper stabilization. Since paper fibers tend to become brittle during ageing, they can be broken easily. If the treatment slows down ageing processes, paper's fibers remain strong and can be separated without damages. Also ageing is normally attributed not only to the cellulose chain scission and changes in functionalities but to the cross-linking and irreversible intermolecular hydrogen bonding of cellulose as well. Due to these processes, the paper structure becomes more compact. Thus, the SEM images of the cross section of samples can be indicative of the paper changes undergone during ageing.

The biggest visual structural differences were noticed of the IP sample after the accelerated thermal degradation (Fig. 7). The unaged inked paper sample (IP_c) was found to be fluffy and lots of fibers were pulled out still intact while the paper fibers of the untreated inked paper sample (IP) became brittle after accelerated ageing and all of the fibers were broken.

Figure 8 shows that a great stabilization effect was achieved by the direct treatment of the paper samples either using organic halide salts with the alkaline buffer

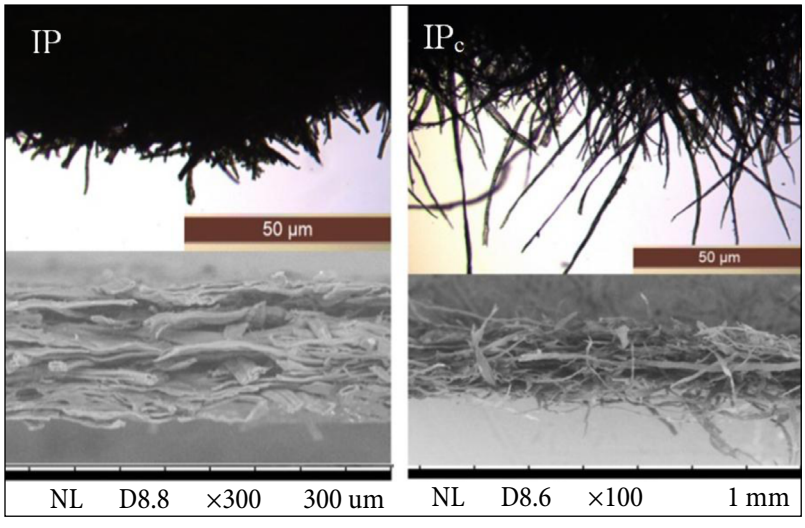

Fig. 7. Optical microscope photographic images of the edge of broken aged and not aged IP samples (top) and scanning electron micrographs of aged paper cross-section (bottom)

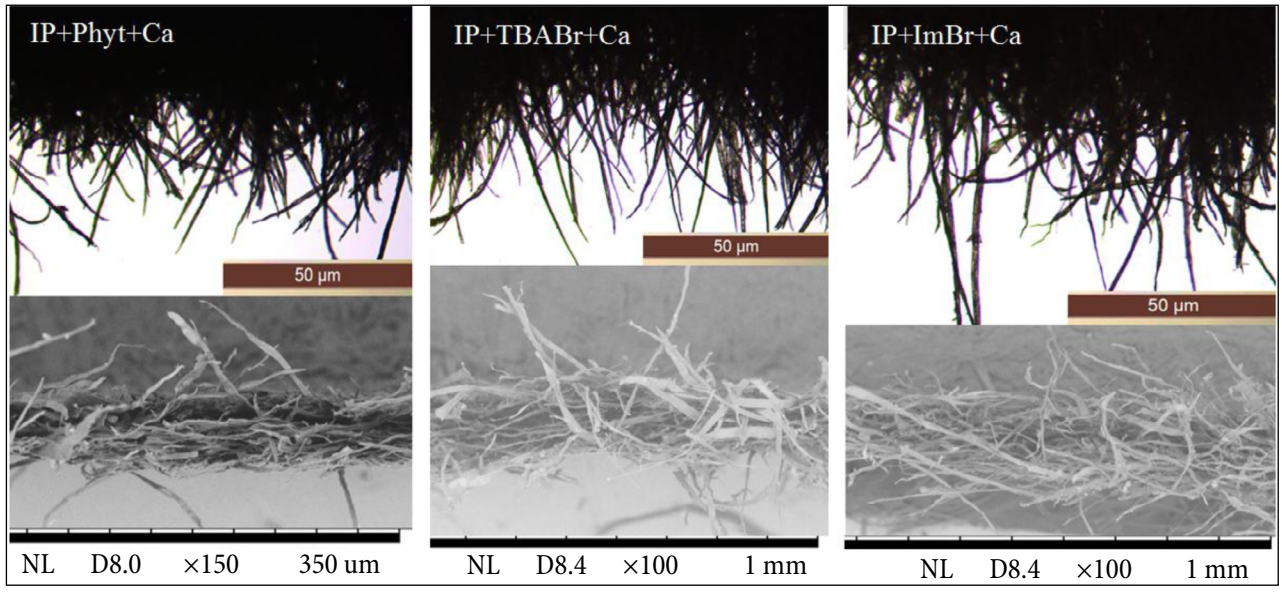

Fig. 8. Optical microscope photographic images of the edge of differently treated and aged broken IP samples (top) and scanning electron micrographs of aged paper cross-section (bottom)

(IP+ImBr+Ca and IP+TBABr+Ca) or applying the calcium phytate/calcium hydrocarbonate treatment (IP+Phyt+Ca). A huge chunk of fibers was pulled out not broken and the paper remained fluffy.

Although the best paper stabilization effect was achieved by the direct treatment, the condition of fibers of some indirectly treated samples remained also nearly changed after ageing. The indirect treatment by interleaving of the inked paper samples between the interleaves charged with KI or KBr with an alkaline buffer (IP□KI+Ca; IP□KBr+Ca) showed a better stabilization effect than that using the interleaves saturated with ImBr and the alkaline buffer (IP□ImBr+Ca) (Fig. 9). In the case of inorganic halides paper remained fluffy and fibers were pulled out almost without lots of damages.

This is also confirmed by paper surface photos pictured by SEM. Figure 10 shows the cracks of several fibers of the aged untreated inked paper sample (IP) while none of similar kind cracks are seen on the fibers of the paper sample indirectly treated with KBr and the alkaline buffer (IP□KBr+Ca).

Evaluation of pH changes

The pH values of differently treated two paper sample sets were measured before and after accelerated ageing. The pH values of the untreated inked paper sample (IP) before and after accelerated ageing are similar because the pH value of paper soaked in an acidic ink before ageing were already below 4 (Fig. 11). According to the results shown in Fig. 11, the pH values of the directly treated inked paper samples

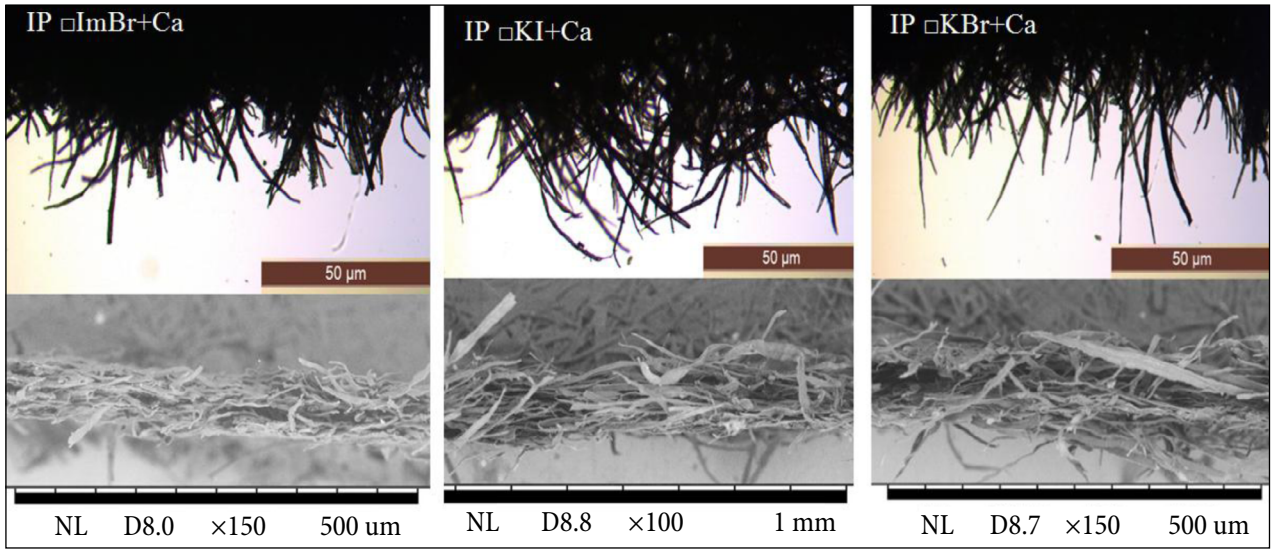

Fig. 9. Optical microscope photographic images of the edge of differently treated and aged broken IP samples (top) and scanning electron micrographs of aged paper cross-section (bottom)

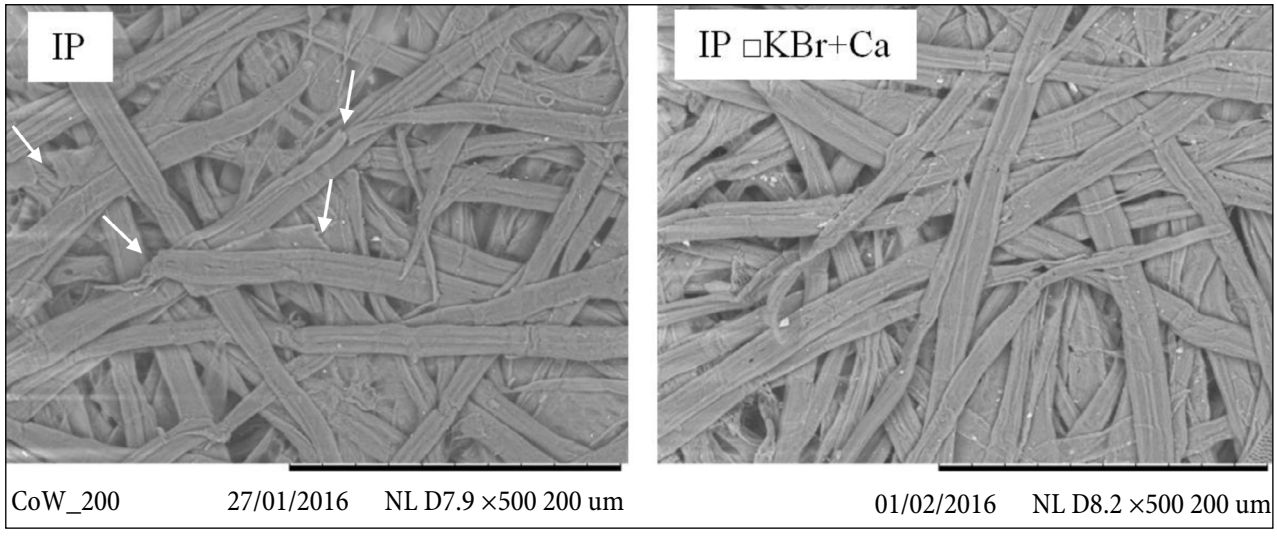

Fig. 10. Scanning electron micrographs of the surface of aged paper samples (arrows show some broken fibers)

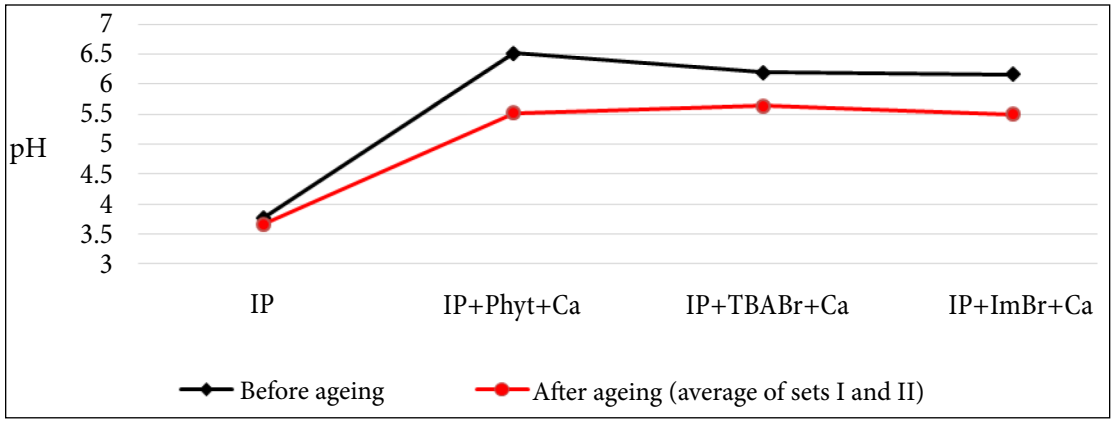

Fig. 11. pH values of IP samples (average of the data of set I and set II) before and after ageing

before accelerated ageing are close to neutral. However, pH values decrease during ageing.

The pH values of the indirectly treated inked paper samples remained unchanged or slightly increased during accelerated ageing (Fig. 12). Most likely, the pH values increased because both an active alkaline buffer and acids could migrate from the interleaves to the paper samples and vice versa. Moreover, the pH values could have increased because of the insertion of alkaline halide salts into samples.

Evaluation of colour changes

Since iron gall ink hides the colour of paper, samples of filter paper soaked just in a 0.01% solution of $FeSO_4 \cdot 7H_2O$ (marked as PFe) were prepared. In this way the samples contain iron ions which promote oxidation of cellulose and the colour of paper remains unchanged. Then, the same stabilization treatments, materials and ageing conditions were applied (Table 1).

Since the colour change of paper during the conservation treatment is undesirable, determination of colour change could do inform both 1) suitability of the chosen stabilization treatment and 2) the stabilization effect during ageing.

The colour change of differently treated and aged PFe samples was compared with the change of the untreated and unaged PFe samples (Table 1). The most considerable colour changes of paper were observed when the direct conservation treatment with TBABr and ImBr without the alkaline buffer (PFe+TBABr; PFe+ImBr) was applied

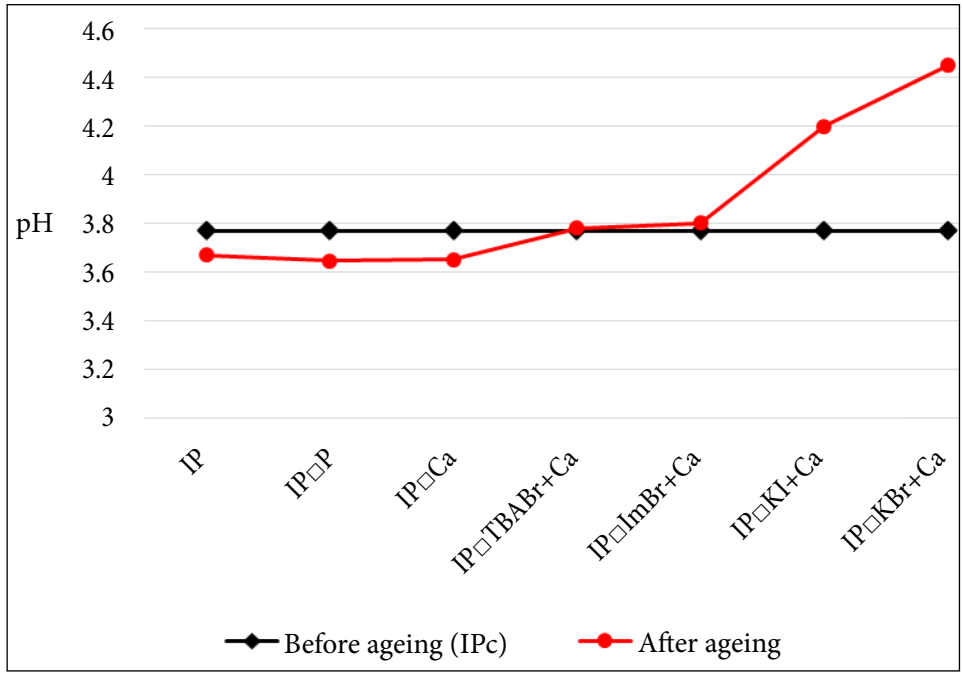

Fig. 12. A comparison of pH values of not aged sample IP_c with those interleaved between differently treated papers and aged (data of set I /set II – averages)

while such colour changes did not appear when the alkaline buffer was added (PFe+TBABr+Ca; PFe+ImBr+Ca) (Fig. 13). Therefore, the alkaline buffer is needed in order to decrease the possibility of paper colour change. Also, a considerable colour change of paper sample was observed when the indirect treatment with the ImBr and alkaline buffer (PFe□ImBr+Ca) was applied (Fig. 13).

The colour change of manuscript's paper during treatment is undesirable because the aesthetics and authenticity of the document may be altered. For this purpose, the colour change of the aged, differently treated dashed paper samples (imitation of manuscripts) was compared with that of an unaged, untreated dashed paper sample (IP'). In this case the colour change was measured around the undashed area of the paper samples.

The results shown in Fig. 14 indicate that the colour change of the dashed paper sample (used to simulate the manuscript) became more perceptible at a glance only after the conservation treatment with the KI and alkaline buffer (IP'□KI+Ca). However, such a colour change possibly may be reduced by charging the interleaves with a less concentrated KI solution. On the other hand, when using the KBr and alkaline buffer for paper stabilization (sample IP'□KBr+Ca) the colour change can be observed only

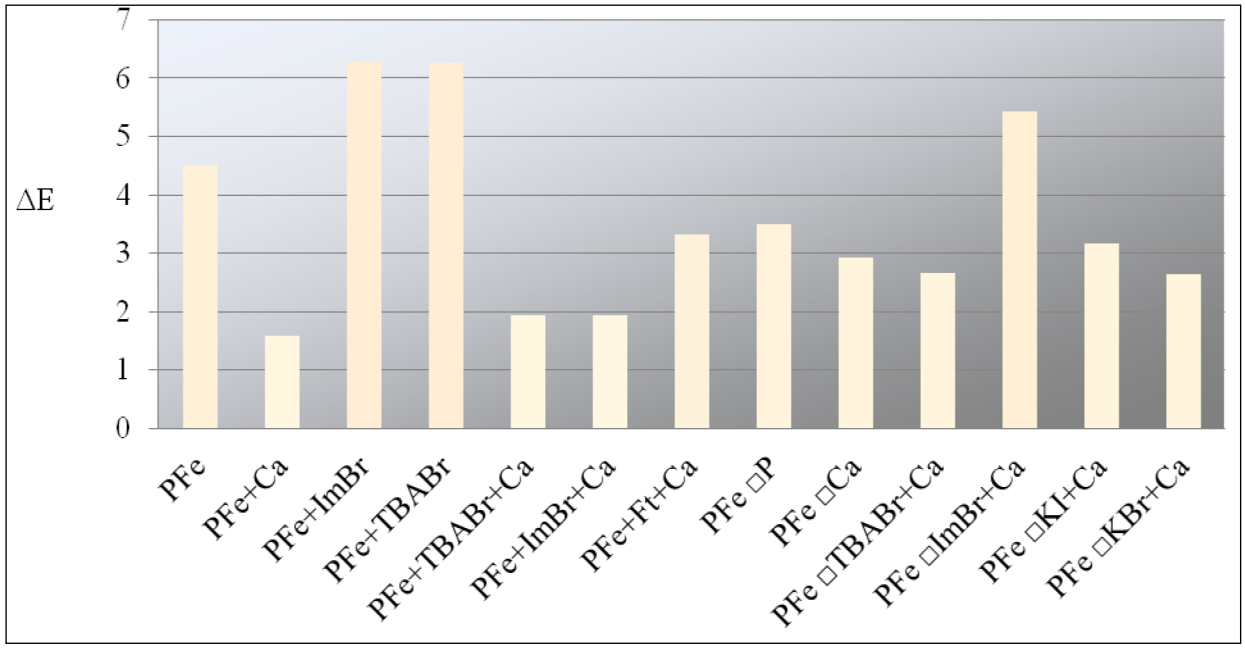

Fig. 13. Colour change of differently treated paper samples with $FeSO_4 \cdot 7H_2O$ after ageing

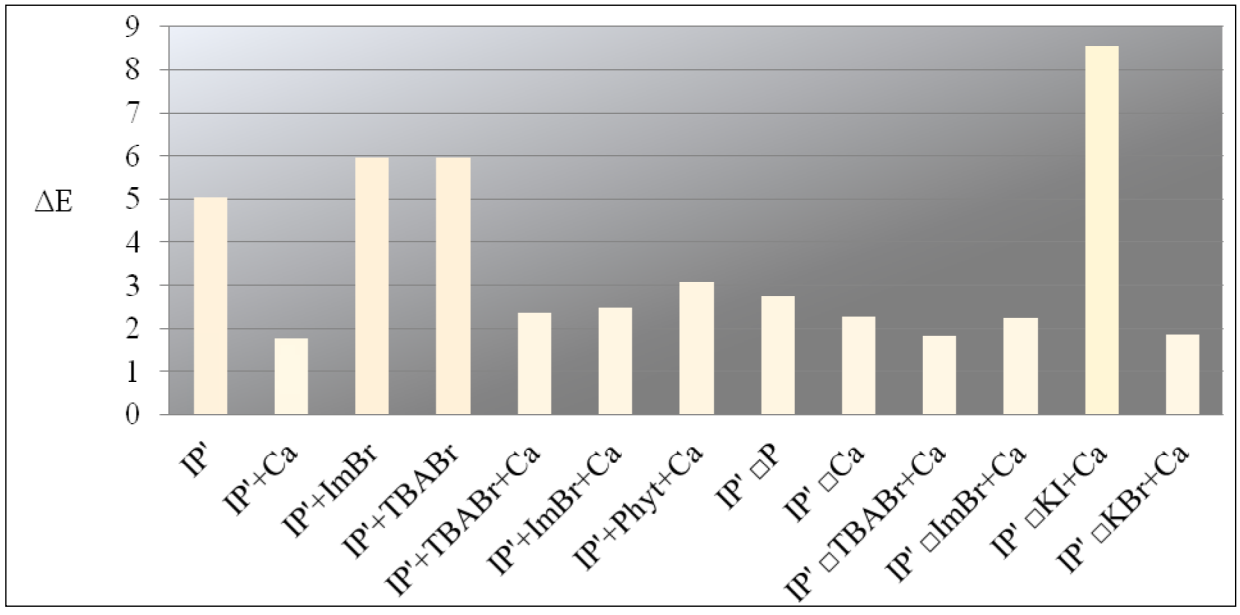

Fig. 14. Colour change of dashed and differently treated paper samples after ageing

through a very close observation which makes the treatment with the KBr and alkaline buffer the fast-track method for the indirect treatment of inked paper.

CONCLUSIONS

The results demonstrate that the most effective stabilization of paper containing iron gall ink is achieved by immersion of the samples in aqueous solutions. However, during the direct treatment the samples of inked paper also showed a pronounced efficiency of stabilization using the antioxidant tetrabutyl-ammonium bromide or 1-ethyl-3-methylimidazolium bromide in ethanol with an alkaline buffer – calcium hydrocarbonate. The research on the efficacy of interleaving on the degradation of samples interleaved with filter papers charged with an inorganic halide salt of potassium bromide with an alkaline buffer showed a better ageing stability than those interleaved with papers containing organic halide compounds. A good stabilization effect was also achieved by interleaving the inked paper samples with interleaves containing potassium iodide and an alkaline buffer. However, usage of this inorganic halide salt can induce the undesirable colour changes of paper.

The results of the indirect treatment are promising as no migration of iron ions from the ink lines to the surrounding paper could be observed. Moreover, no major changes in the ink colour or paper colour were observed after the treatments or after the accelerated thermal ageing. The effect of paper stabilization was proved as well as the increase of pH towards alkaline values.

The proposed procedures of the indirect treatment show encouraging results. However, the investigation has to be continued in order to determine the reliance between the interleaving treatment efficiency and the concentration of an antioxidant in interleaves before it can be considered a safe treatment on authentic historical documents.

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ORGANINIŲ IR NEORGANINIŲ HALOGENIDŲ POVEIKIO POPIERIAUS SU GELEŽIES-GALO RAŠALU SENĖJIMUI STABDYTI TYRIMAS

S a n t r a u k a

Imituojant istorinius rankraščius buvo paruošti celiuliozės popieriaus bandiniai su pagal senovinio geležies-galo rašalo receptūrą pagamintu modeliniu rašalu. Viena dalis bandinių tiesiogiai apdorota organiniais halogenidais (tetrabutilamonio bromidu, 1-etil-3-metilimidazolio bromidu), neorganiniais halogenidais (kalio jodidu, kalio bromidu) ir šarmine medžiaga – kalcio karbonatu. Kita dalis bandinių apdorota netiesiogiai: bandiniai patalpinti tarp kontaktinių lakštų, turinčių kalcio karbonato ir atitinkamai apdorotų tetrabutilamonio bromidu, 1-etil-3-metilimidazolio bromidu bei kalio bromidu ir kalio jodidu. Siekiant įvertinti skirtingo apdorojimo efektyvumą ir palyginti apdorojimui naudotų junginių bei apdorojimo metodo įtaką stabdant popieriaus senėjimą, apdoroti ir neapdoroti bandiniai buvo dirbtinai termiškai pasendinti. Sendinti bandiniai buvo tirti nustatant popierių sudarančios celiuliozės polimerizacijos laipsnį (viskozimetrijos ir molekulinių sietų chromatografijos metodais), išmatuojant pH vertes, popieriaus spalvos pokyčius. Popierių sudarančių plaušų būklei įvertinti skleidžiamuoju elektroniniu mikroskopu nufotografuotas bandinių paviršius bei skerspjūvis, o optiniu mikroskopu – perplėštų bandinių trūkio sritis.

Nustatyta, kad bandiniai su geležies-galo rašalu buvo stabilizuojami ir jų tiesiogiai neapdorojant. Netiesioginio apdorojimo metodas buvo efektyviausias naudojant kontaktinius lapus su $CaCO_3$ ir KBr.

Kadangi konservavimo procese tiesioginio apdorojimo procedūra siejama su galimais nepageidautinais autentiškų dokumentų pokyčiais, netiesioginio apdorojimo metodas ypač reikalingas konservuojant istorinius rankraščius.