VILNIUS UNIVERSITY

Birutė Sivakova

THE INVESTIGATION OF THE DEGRADATION OF INKED PAPER AND THE EVALUATION OF NEW CONSERVATION TECHNIQUES

Summary of doctoral dissertation
Physical sciences, Chemistry (03 P)

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The work was carried out in Vilnius University in the period 2005–2009.

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VILNIAUS UNIVERSITETAS
FTMC CHEMIJOS INSTITUTAS

Birutė Sivakova

POPIERIAUS SU RAŠALU IRIMO PROCESO TYRIMAS IR NAUJŲ KONSERVAVIMO METODŲ ĮVERTINIMAS

Daktaro disertacijos santrauka
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1. INTRODUCTION

One of the most popular materials to write and save information on is paper. Various printed or written documents from different periods of time constitute bigger part of written heritage that is stored in libraries and archives. A lot of valuable historical manuscripts are written using metallo-gallic ink which was particularly popular in Europe for many centuries. Letters of well-known people, prominent music pieces, official documents, court books, maps and even some works of famous artists were created using metallo-gallic ink.

Today the duty of librarians and archivists is not only to preserve the written heritage but to ensure that the information written on paper would be easily approachable as well. Paper is a well known and commonly used medium; nevertheless it is a very complex and unhomogeneous material. Thus, the problem of preservation of written documents is especially significant. As sorts of paper used to create various documents differ, so does the problems related with paper preservation. To warrant qualified restoration and preservation of written documents means not only to have general knowledge about the decay of paper and its' stabilization but to be aware of the impact of writing material on paper support, to know the document research techniques and methodologies and to be informed on how to monitor the results of newest conservation techniques as well. To preserve written heritage, especially in such cases were metallo-gallic ink was used, is a real challenge to the conservation scientists and to those who takes on practical restoration. Finding out the reason and nature of the decay of such documents is complicated by many factors, namely: unknown age, composition and the way of manufacturing of the ink that was used to write on the document, vague knowledge of possible previous conservation techniques and the conditions in which the document was stored for many years.

Restoration and preservation of historical manuscripts delivers many problems as it is not always easy to establish that metallo-gallic ink was used. Moreover, the components of the ink and the impact that they have on paper medium must be recognized in order to select suitable conservation technique and correctly predict its' effectiveness. Eventually, huge amount of disintegrating manuscripts is an issue hard to solve because of the selection of conservation techniques becomes even more difficult.

Conservators have to evaluate the state of whole collections and select those that require immediate conservation.

Seeking to make damaged documents available to user again conservators have to foresee and evaluate all risks and possible changes that could affect the authenticity of the document or stipulate the alteration of written information. The risks are evaluated in the context of the characteristics, state and future usage of the document in mind. Thus the instructions of restoration should include as many techniques as possible. In that way restorers would be allowed to take into consideration the individuality of the document and be more specific about the issues related to it.

The main aim of this work was to investigate the influence of ink composition on the degradation of cellulose paper and to evaluate the impact of alkalisation and antioxidant treatment on ageing resistance of inked paper. For this reason there were formulated tasks as follows:

1. Investigation of the impact of eight model inks prepared according to ancient recipes on the degradation of cotton and eucalyptus cellulose paper.
2. Development of the technique for deacidification treatment of paper by non-aqueous systems of calcium and magnesium compounds and solution of 3-aminopropyltrietoxysilane (APTES).
3. Investigation of the effect of new system APTES/KI (3-aminopropyltrietoxysilane (APTES)) as the deacidification agent together with KI as an antioxidant) on the ageing stability of inked paper.
4. Investigation of the impact of ageing conditions on the degradation of inked paper and the evaluation of the effect of system APTES/KI as the agent for passive conservation.

Statements for defence:

1. Various inks have the degrading effect on cotton and eucalyptus cellulose paper. The degradation of paper is particularly accelerated by inks with transition metal ions.
2. The character of deterioration of paper depends on the nature of its main constituent – cellulose – and previous processing of raw fibers. The intensity of deterioration depends on the ageing conditions of inked paper.

3. After deacidification of paper by the dispersions of nanoparticles of $Ca(OH)_2$ and $Mg(OH)_2$, calcium compounds are inserted into paper in larger quantities, though the alkalinity of $Mg(OH)_2$ treated paper is higher.
4. The deacidification treatment of paper with APTES solution in 2-propanol meets the main requirements of paper deacidification procedures: the obtained alkaline reserve and the pH value of the paper become proper after treatment.
5. The stabilization system APTES/KI has a positive effect on the stability of inked paper: the process of paper degradation during accelerated ageing is slowed down due to treatment of soaking in APTES/KI solution and through usage of such system in the manner of passive conservation.
6. The development of the stabilization system APTES/KI for stabilization of historical manuscripts may be under consideration.

2. EXPERIMENTAL

2.1 Materials and reagents

For the preparation of inks and paper stabilization systems analytical grade reagents were used. All chemicals were used as purchased without any additional purification.

2.2. Synthesis of deacidification agents

2.2.1. Synthesis of calcium hydroxide

Calcium hydroxide was obtained by mixing equal volumes of aqueous solutions of NaOH and $CaCl_2 \cdot 2H_2O$. Separately prepared aqueous solutions: 100 ml of 0.8M NaOH and 100 ml of 0.4M $CaCl_2 \cdot 2H_2O$ were heated separately. When the temperature has reached 85°C, two solutions were rapidly mixed under stirring keeping the temperature of the mixture constant within 1 °C. The $Ca(OH)_2$ suspension was allowed to reach room temperature under a nitrogen atmosphere to avoid carbonation. The supernatant solution was separated and the suspension was washed 5 times by water to remove NaCl. The complete removal of NaCl from the suspension was controlled by $AgNO_3$ tests. The suspension was then concentrated in a vacuum at 40 °C up to a 0.8 $Ca(OH)_2$/water weight ratio.

2.2.2. Synthesis of magnesium hydroxide

Magnesium hydroxide was obtained by mixing equal volumes of aqueous solutions of NaOH and $MgSO_4$. Separately prepared aqueous solutions: 100 ml of 2M NaOH and 100 ml of 1M $MgSO_4$ were heated separately. When the temperature has reached 85°C, two solutions were rapidly mixed under stirring keeping the temperature of the mixture constant within 1 °C. The $Mg(OH)_2$ suspension was allowed to reach room temperature under a nitrogen atmosphere. The supernatant solution was separated and the suspension was washed 5 times by water to remove NaCl. The complete removal of NaCl from the suspension was controlled by $AgNO_3$ tests. The suspension was then concentrated in a vacuum at 40 °C

2.3. The recipes of inks and stabilization systems

2.3.1. The recipes of inks

Eight different model inks were prepared according to following ancient recipes.

1. Pfalz ink with red wine: 100 ml of red wine was mixed with 5.0 g of powdered cherry gum and 4.0 g of soot was added. The mixture was stored for 2 weeks (with daily shaking) in a closed flask.

2. Ink from oak bark: 61.0 g of crushed oak bark was mixed with 610 ml of distilled water and left for three days. The mixture obtained was boiled for 4 hours and filtered after cooling. Then 30 ml of red wine was added and the volume of obtained solution was reduced up to 50 ml by slow evaporation.

3. Iron-gall ink: 1.0 g of powdered oak galls, 1 ml of 10 % acetic acid, 0.53 g of iron(II) sulphate $FeSO_4 \cdot 7H_2O$ and 0.53 g of grinded gum arabic were added to 16 ml of cold distilled water. The mixture was stored with mixing in covered vessel for 8 weeks.

4. Black ink with iron(II) sulphate: 7.68 g powdered oak gall nuts was mixed with 66.8 ml of distilled water. The mixture was stored for 3 days. To this 2.52 g of iron(II) sulphate, 0.20 g of sodium chloride, 2 ml of 10 % acetic acid and 0.32 g of alum ($KAl(SO_4)_2 \cdot 12H_2O$) were added. The obtained mixture was stored for 2 weeks with intermediate mixing and then filtered.

5. Black ink with copper(II) sulphate: 7.68 g of powdered oak gall nuts was mixed with 66.8 ml of distilled water. The mixture was stored for 4 days. To this 2.52 g of copper(II)

sulphate ($CuSO_4 \cdot 5H_2O$), 0.20 g of NaCl, 2 ml of 10 % acetic acid and 0.31 g of alum were added. The obtained mixture was stored for 2 weeks (with mixing) and filtered.

6. Logwood ink: 100 ml of distilled water, 20.0 g of logwood extract, 1.5 g of gum arabic and 0.1 g of chromium alum ($(KCr(SO_4)_2 \cdot 12H_2O)$) were carefully mixed. After four days the obtained mixture was filtered.

7. German recipe A: 50 ml of distilled water, 4.0 g of gallic acid ($(HO)_3C_6H_2COOH$), 1.0 g of gum arabic and 1,0 g of iron(II) sulphate were carefully mixed. After three days the obtained mixture was filtered.

8. German recipe B: 100 ml of distilled water, 0.7 ml of 10 % hydrochloric acid, 0.77 g of gallic acid, 1.0 g of gum arabic, 2.34 g of tannin, 0.1 g of phenol and 3.0 g of iron(II) sulphate were carefully mixed. After three days the obtained mixture was filtered.

2.3.2. The recipes of stabilization systems

Dispersions of calcium hydroxide and magnesium hydroxide particles were prepared by mixing 10g of obtained $Ca(OH)_2$ or $Mg(OH)_2$ with 1000 ml of 2-propanol, ethanol or butanol in ultrasonic bath (15min). The aqueous solution of $Ca(OH)_2$ was prepared by dissolution of 1.85 g of $Ca(OH)_2$ in 1000 ml of distilled water. APTES solution has been prepared by dissolution of 6 g of 3-aminpropyltriethoxysilane (APTES) in 100 ml of 2-propanol. The solution of antioxidant – potassium iodide – was prepared by dissolution of 3 g of KI in 10 ml of distilled water and mixing with 300 ml of 2-propanol.

2.4. Preparation of samples for investigation

2.4.1 Preparation of model paper

The hand sheets (leaf-casted sheets*)* from pure cotton fibers and chemical pulp of eucalyptus were prepared for the experiment. Paper was made without the presence of fillers, sizing or any other additives. The sheets were formed by leaf casting machine (*Leafcaster)* designed by Danish paper conservator and engineer Per M. Laursen. Two types of leaf-casted paper were prepared for the experiment: paper consisting from pure cotton fibres (average length ~10–40 mm) and paper consisting from sulphate hardwood cellulose (eucalyptus) fibres (average length ~1 mm). The grammage of each type of paper is 70 g/m^2. The leaf-casted paper was made using an aqueous suspension of cellulose fibres. Each sheet of paper was formed on a synthetic net in the leaf-casting machine and then placed on the suction table to remove the excess of water. The wet

sheets of paper were placed for pressing between the sheets of non-woven synthetic material and blotter paper. The moistened blotter paper was replaced several times until the sheets of leaf-casted paper became completely dry. The dried samples were pressed in the screw-press between the sheets of blotter paper for 10 days.

2.4.2. Preparation of samples of inked and stabilized paper

The paper samples were evenly inked using eight different writing inks and allowed to dry at room temperature. Samples of pure and inked paper were soaked in stabilization systems for 30 min. and allowed to dry at room temperature.

2.4.3. Accelerated ageing of samples

Thermal ageing and ageing by ultraviolet (UV) rays was applied. The thermal ageing was performed in different ways. The samples of one set were aged in open vessels in oven at 105 °C for 90 days. The samples of other set were sealed in glass ampoules and aged in oven at 80 °C for 90 days. The samples of the third 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 and aged in an oven at 80 °C for 90 days.

2.5. Apparatus and characterization

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 (0.02 g) was suspended in 1 ml of distilled water. The pH meter Mettler-Toledo MP220 was employed for measuring pH values of suspensions.

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 FTIR measurements were performed using a Perkin-Elmer spectrometer (Spectrum BX II) using standard KBr pellet technique. A total of 20 scans were taken for each sample between 500 $cm^{-1}$and 4000 cm^{-1}, with a resolution of 4 cm^{-1}. The paper samples were pre-heated 1h at 120^{o}C, then paper fibres were chopped roughly to length less than 1 mm and mixed with 100 mg of KBr and pressed into a pellet for FTIR measurement. The area of the CH vibration band (2900 cm^{-1}) of the initial spectrum,

namely, the integral in the frequency range 2800–3000 cm^{-1} was the normalization factor for all absorbance values.

The X-ray powder diffraction (XRD) measurements were performed on a STOE diffractometer operating with $CuK\alpha_1$ radiation. The morphology and microstructure of paper samples were examined by scanning electron microscopy (SEM) on an EVO 50 XVP scanning electron microscope.

3. RESULTS AND DISCUSSION

3.1. The investigation of the impact of ink composition and ageing conditions on the degradation of paper

In this part a systematic investigation of paper samples inked by eight historical writing inks was performed using IR spectroscopy, the determination of pH of paper and the degree of polymerization of cellulose.

3.1.1. The investigation of paper degradation by estimation of polymerization degree of cellulose

The polymerization degree of cellulose of pure cotton and eucalyptus paper and paper with inks (1–8) was determined before and after accelerated ageing. From the results it is evident that inks promote degradation of cellulose. The polymerization degree of cellulose of papers with ink 3, 4, 5 and 8 was hardly declined. Irradiation of inked cotton and eucalyptus paper by UV rays is a more significant degradation factor comparable to the thermal ageing of the same type of paper (Fig. 1).

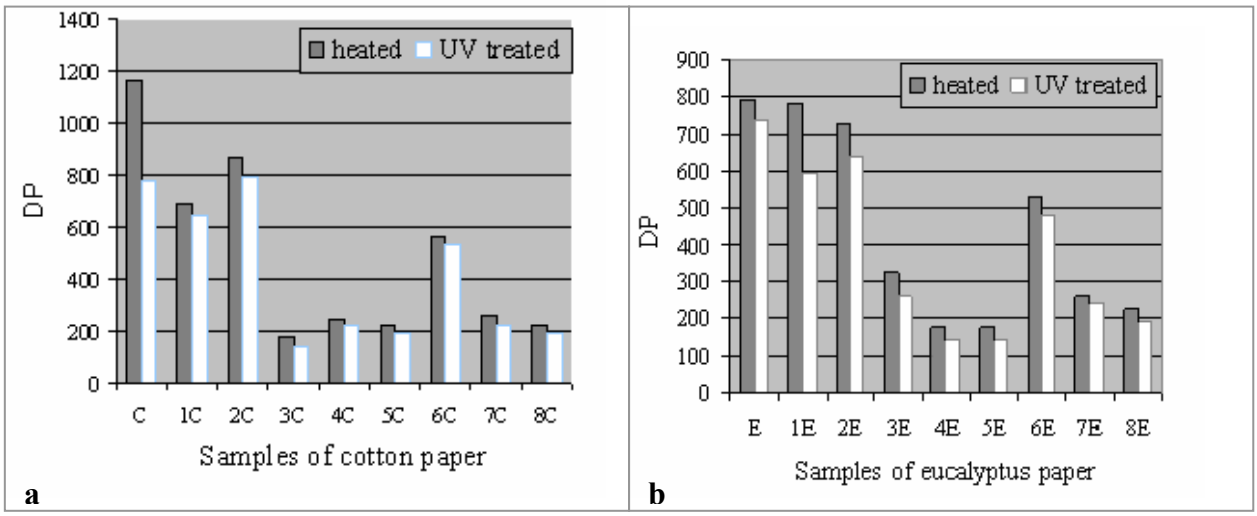


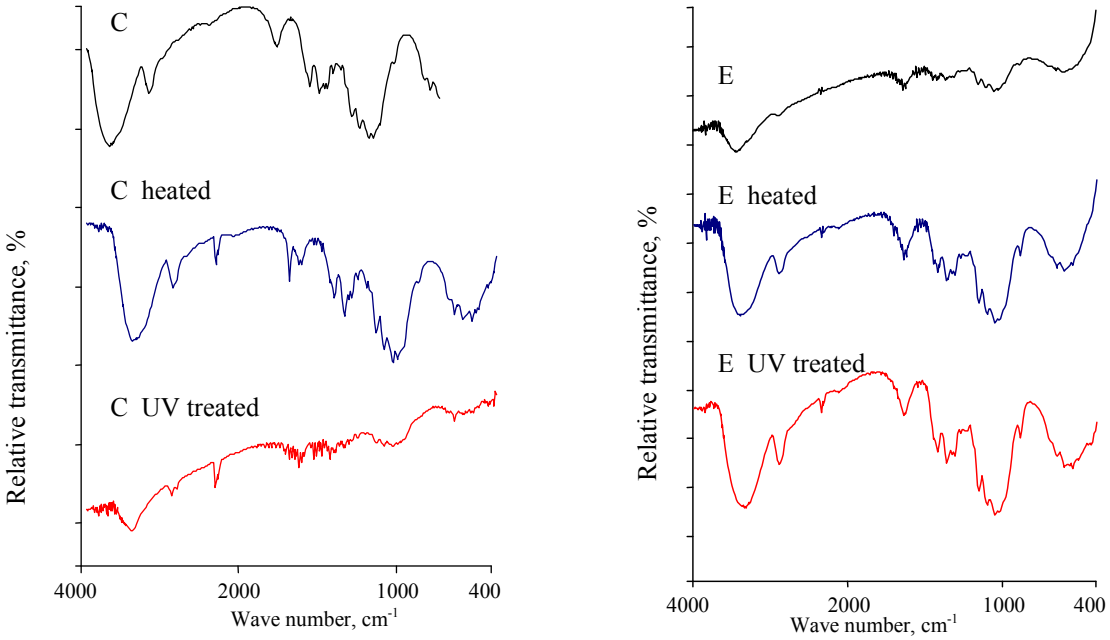
Fig. 1. Polymerization degree of cellulose of thermally aged paper (heated) and irradiated by UV rays (UV treated): a) cotton paper(C); b) eucalyptus cellulose paper (E). The inked paper samples are marked with numbers corresponding to inks 1–8.

3.1.2. The investigation of paper degradation by estimation of pH values of paper

Determination of pH values of inked paper before and after thermal accelerated ageing have been performed as well as before and after irradiation by UV rays. The acidity of samples was influenced minutely by accelerated ageing and increase of pH values has been established in most cases. Such results may be influenced by removal of volatile organic compounds from the samples during accelerated ageing.

3.1.3. The investigation of paper degradation by IR spectroscopy

In this part an investigation of cotton and eucalyptus cellulose paper samples before and after accelerated ageing was performed using IR spectroscopy (thermal accelerated ageing (720 h at 105ºC) and irradiation by UV rays for 100 h was applied). The cotton and eucalyptus paper samples give similar FTIR spectra (Fig. 2) very close to pure cellulose spectra: the broad absorptions in all spectra around 1640 cm^{-1} indicate the presence of adsorbed water on the surface of samples, as all samples were pre-heated 1h at 120 °C before measurements. The bands at ca. 2360-2340 cm^{-1} presented in the spectra belong to carbon dioxide adsorbed from atmosphere.



a **b**

Fig. 2. The IR spectra of not aged, thermally aged (heated) and UV irradiated (UV treated) paper: a) cotton paper (C); b) eucalyptus cellulose paper (E)

The peaks at 1429 cm^{-1} (CH_2 stretch), at 1370 cm^{-1} and 1320 cm^{-1} (C-H and C-OH bending), at 1163 cm^{-1} (C-O-C stretching) are the characteristic peaks of cellulose samples. However, according to the origin of the bands, it is established that aged samples of cotton and eucalyptus are different regarding their carbonyl group peaks intensity. IR spectrum of aged cotton sample contains the more intensive bands attributable to -CO and -CHO stretching at around 1713 cm^{-1} and 1733cm^{-1}.

The inked paper samples were investigated before and after accelerated ageing. The study focus was on the spectra between 1900 cm^{-1} and 1500 cm^{-1} where products of cellulose degradation appear as various carbonyl groups absorptions (Fig. 3–10).

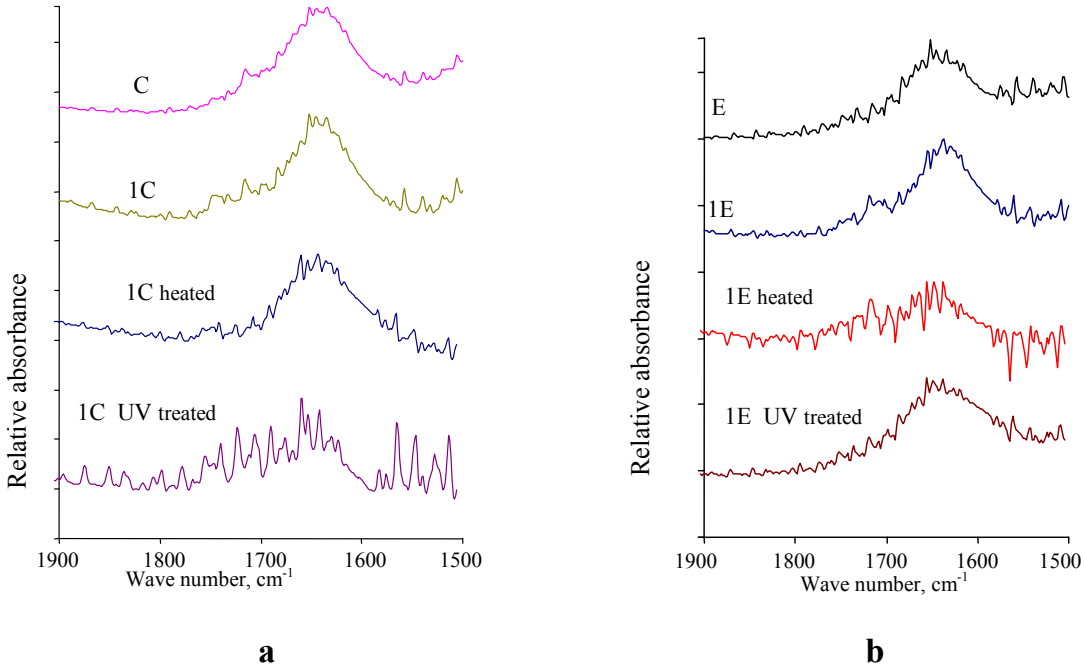


Fig. 3. The IR spectra of not aged, thermally aged (heated) and UV irradiated (UV treated) paper: a) cotton paper (C); b) eucalyptus cellulose paper (E). 1C and 1E indicates cotton paper and eucalyptus cellulose paper inked with ink 1

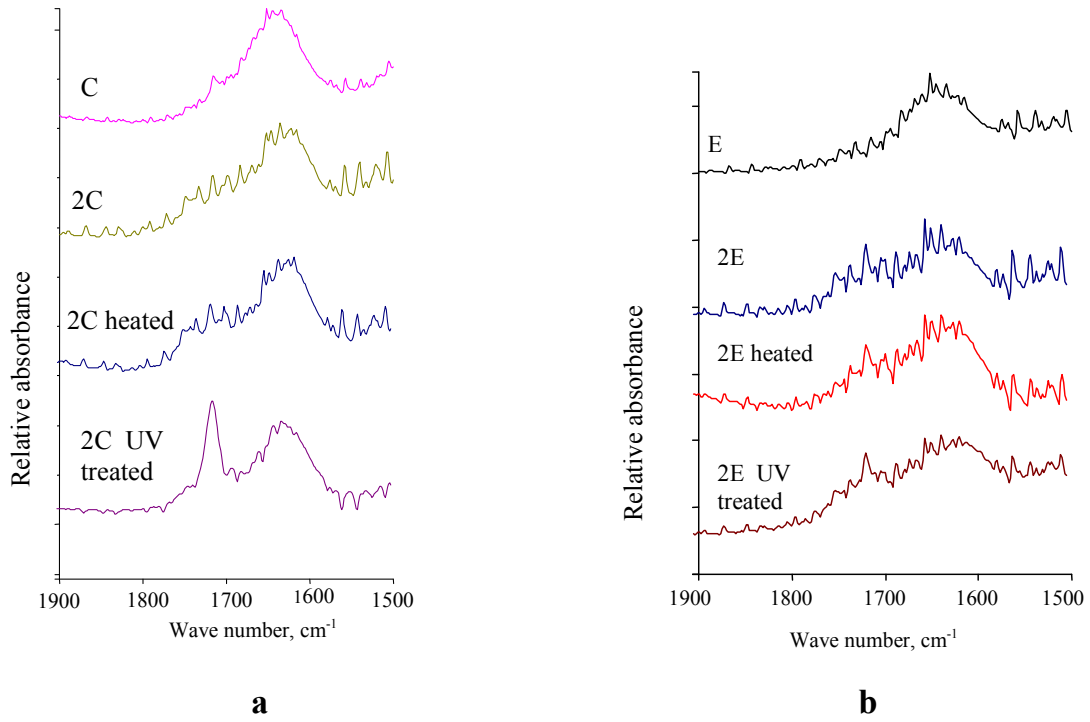


Fig. 4. The IR spectra of not aged, thermally aged (heated) and UV irradiated (UV treated) paper: a) cotton paper (C); b) eucalyptus cellulose paper (E). 2C and 2E indicates cotton paper and eucalyptus cellulose paper inked with ink 2

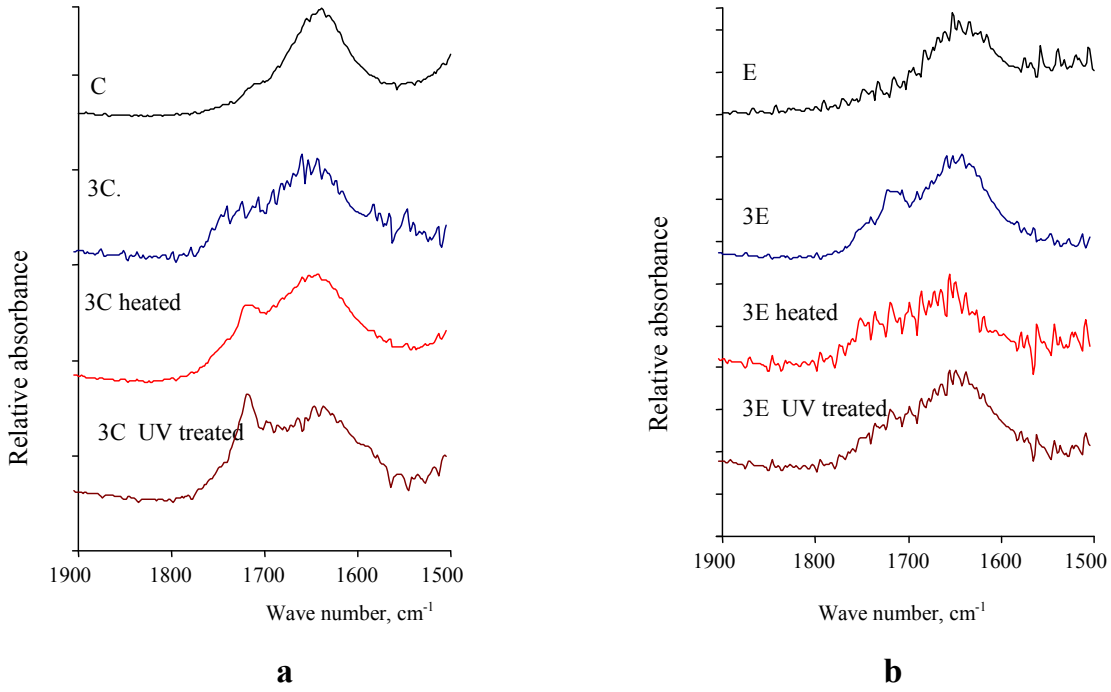
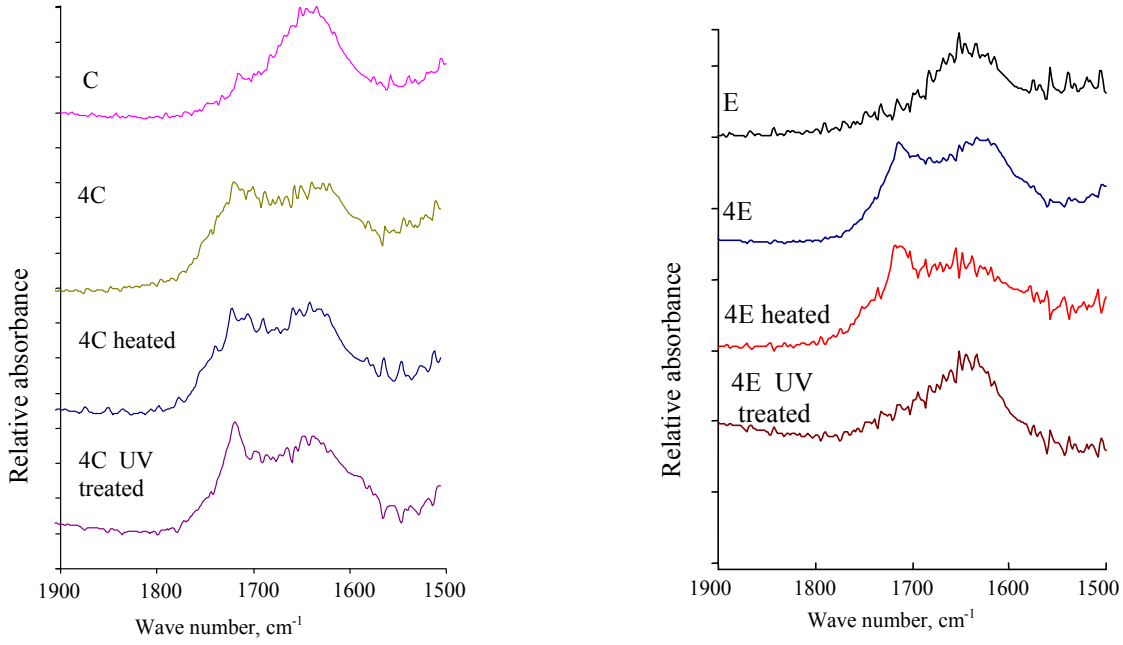
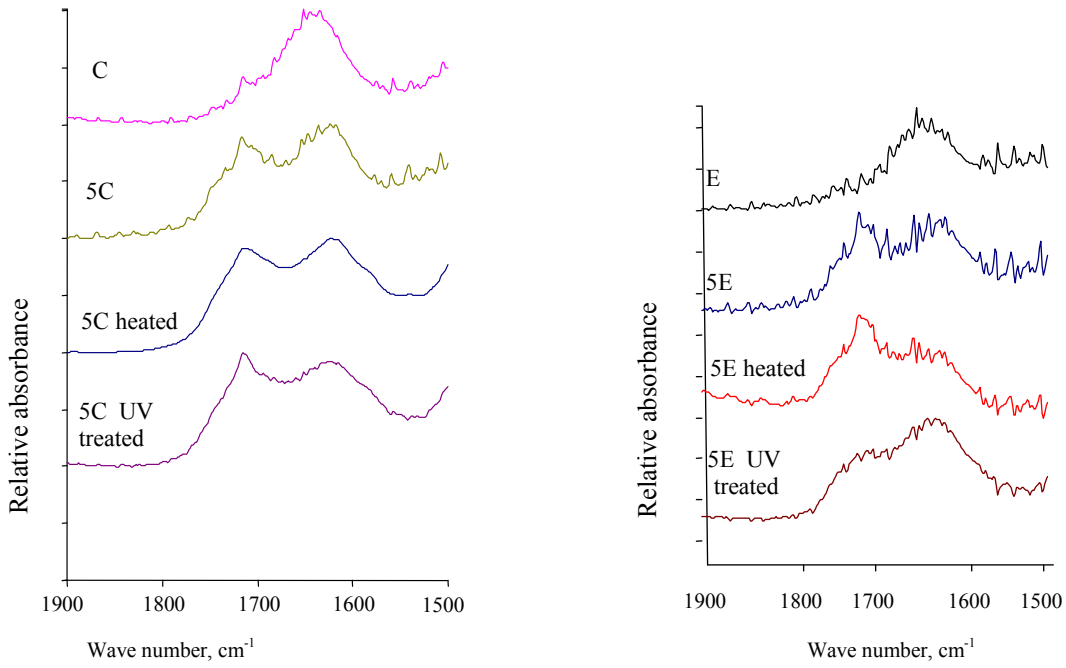


Fig. 5. The IR spectra of not aged, thermally aged (heated) and UV irradiated (UV treated) paper: a) cotton paper (C); b) eucalyptus cellulose paper (E). 3C and 3E indicates cotton paper and eucalyptus cellulose paper inked with ink 3



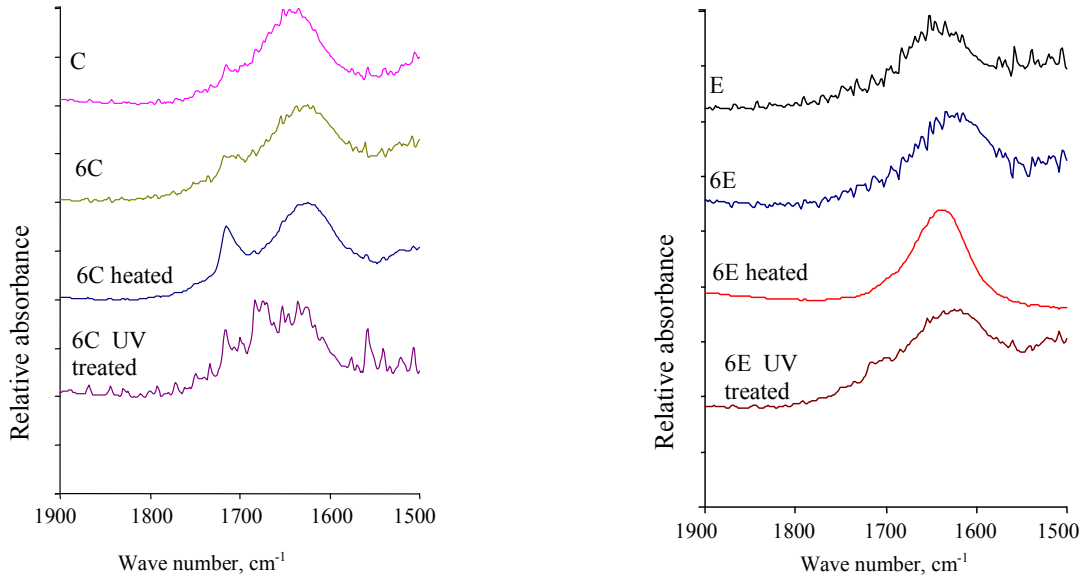
a **b**

Fig. 6. The IR spectra of not aged, thermally aged (heated) and UV irradiated (UV treated) paper: a) cotton paper (C); b) eucalyptus cellulose paper (E). 4C and 4E indicates cotton paper and eucalyptus cellulose paper inked with ink 4



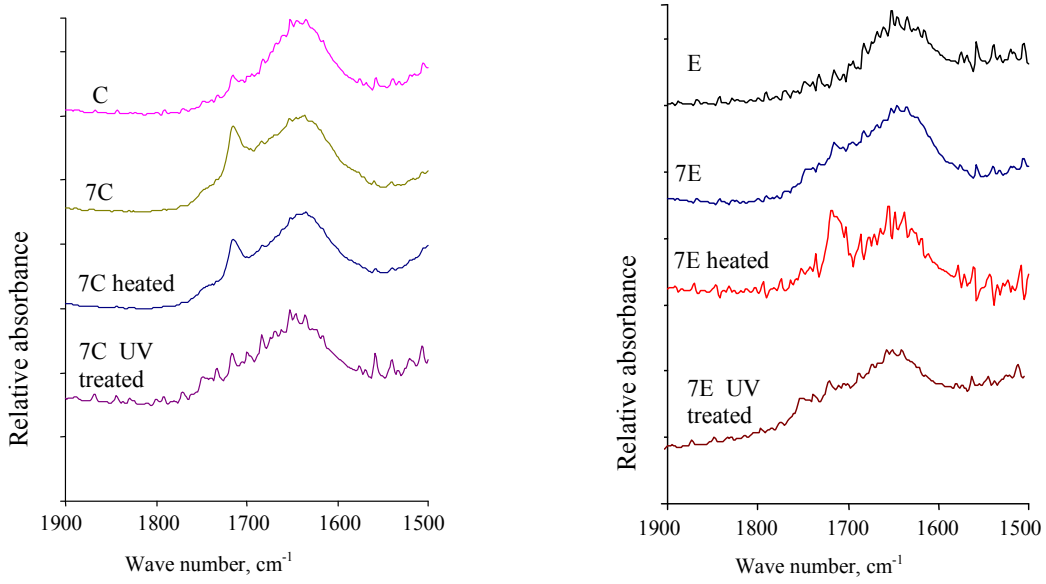
a **b**

Fig. 7. The IR spectra of not aged, thermally aged (heated) and UV irradiated (UV treated) paper: a) cotton paper (C); b) eucalyptus cellulose paper (E). 5C and 5E indicates cotton paper and eucalyptus cellulose paper inked with ink 5



a **b**

Fig. 8. The IR spectra of not aged, thermally aged (heated) and UV irradiated (UV treated) paper: a) cotton paper (C); b) eucalyptus cellulose paper (E). 6C and 6E indicates cotton paper and eucalyptus cellulose paper inked with ink 6



a **b**

Fig. 9. The IR spectra of not aged, thermally aged (heated) and UV irradiated (UV treated) paper: a) cotton paper (C); b) eucalyptus cellulose paper (E). 7C and 7E indicates cotton paper and eucalyptus cellulose paper inked with ink 7

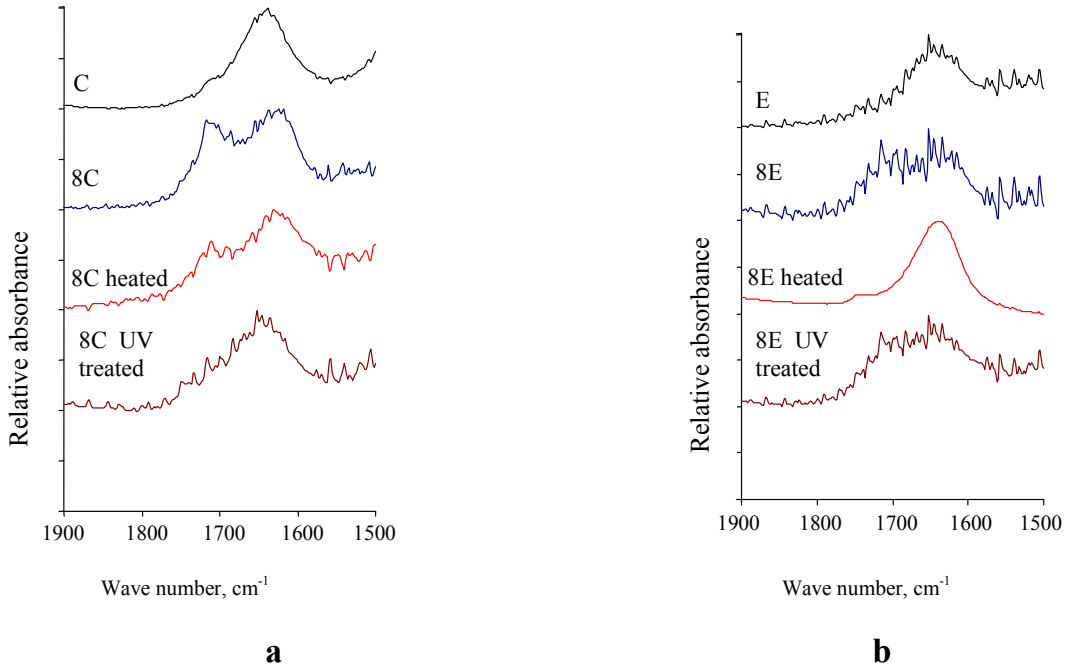


Fig. 10. The IR spectra of not aged, thermally aged (heated) and UV irradiated (UV treated) paper: a) cotton paper (C); b) eucalyptus cellulose paper (E). 8C and 8E indicates cotton paper and eucalyptus cellulose paper inked with ink 8

The observation of the increasing of carboxyl and carbonyl peaks located at 1733 cm^{-1}, 1685cm^{-1} and 1620 cm^{-1} of inked samples seems to indicate that hydrolysis and oxidation reactions ran during ageing. Infrared spectra of cotton and eucalyptus paper without and with ink were compared. One of the most visible differences between the spectra was the modification of the signal at 1713 cm^{-1}, characteristic of the stretching of unconjugated CO groups. This peak appeared after treatment with all inks, but is weaker for papers treated with ink 1, 2, and 6. While the high intensity of this peak was observed for samples treated with ink 3, 4, 5 and 8.

The data of evaluated spectra show, that the presence of metal ions and low pH value of ink accelerated formation of carbonyls. The most intensity of carbonyl band at 1713 cm^{-1} were registered for eucalyptus paper samples with ink 4, 5, 7 and 8 where metal ions were presented.

3.2. Study of non-aqueous deacidification systems with traditional agents for paper alkalization and the investigation of the impact of APTES for the stabilization of paper

The efficiency of non-aqueous systems for paper deacidification using $Ca(OH)_2$, $Mg(OH)_2$ nanoparticles in 2-propanol and solution of 3-aminopropyltriethoxysilane (APTES) in 2-propanol have been evaluated by determination of pH values of paper, alkali reserve (a.r.) and by analysis of SEM/EDX. Three different types of paper: leaf-casted cotton (pH 6.50) and eucalyptus paper (pH 6.78) as well as old acidic paper (pH 5.23) from XIX century have been tested.

3.2.1. The modification and investigation of properties of $Ca(OH)_2$ and $Mg(OH)_2$ The search of solvent for non-aqueous systems.

The main objective of the present study was to synthesize the $Ca(OH)_2$ and $Mg(OH)_2$ nanoparticles and to prepare the non-aqueous systems for paper deacidification. The synthesis of $Ca(OH)_2$ and $Mg(OH)_2$ nanoparticles has been performed according to preparation procedure described in literature. The $Ca(OH)_2$ and $Mg(OH)_2$ was obtained by the following reactions:

$$2NaOH + CaCl_2 \cdot 2H_2O \rightarrow Ca(OH)_2 + 2NaCl + H_2O$$

$$MgSO_4 + 2NaOH \rightarrow Mg(OH)_2 + Na_2SO_4$$

The IR spectroscopy and X-ray diffraction analysis have been performed in assessing the chemical composition of formed products.

For the preparation of non-aqueous dispersions of $Ca(OH)_2$ and $Mg(OH)_2$ the ethanol, 2-propanol and 1-butanol have been used. Dispersions in water have been prepared for the comparison. The pH values of all dispersions are shown in Fig. 11.

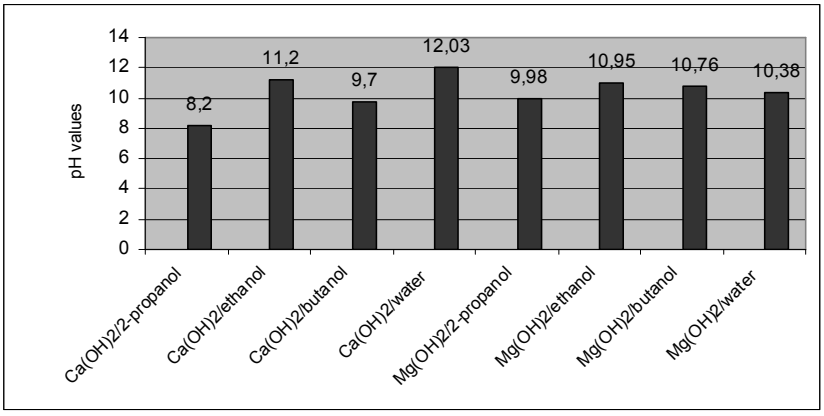


Fig. 11. The pH values of $Ca(OH)_2$ and $Mg(OH)_2$ in different solvents.

2-Propanol has been selected for preparation of deacidification systems because the pH values of suspensions of $Ca(OH)_2$ and $Mg(OH)_2$ in 2-propanol do not exceed 10.

3.2.2. The investigation of the effectiveness of paper alkalization

The samples of cotton paper (C), paper from eucalyptus cellulose (E) and historical paper from XIX century (G) treated by $Ca(OH)_2$ and $Mg(OH)_2$ dispersions in 2-propanol as well as in solution of APTES have been investigated. The pH values of treated samples and the amount of alkaline compound inserted have been determined. The IR spectroscopy has been performed to evaluate changes of functionalities of treated and non treated paper after accelerated ageing.

3.2.2.1. The determination of pH values of paper

To verify the efficiency of deacidification treatment the pH values of paper samples have been determined according to ISO 6588-1 method before and after thermal ageing (30 days at 105 °C).

Table 1. The pH values of eucalyptus (E), cotton (C) and historical paper (G) before ageing

Paper sample	The pH values of paper			
	Before treatment	After treatment by		
		$Ca(OH)_2$ in 2-propanol	$Mg(OH)_2$ in 2-propanol	Solution of APTES in 2-propanol
E	6.78	8.60	8.76	9.04
C	6.50	8.94	8.84	9.07
G	5.23	6.48	6.42	6.55

Table 2. The pH values of eucalyptus (E), cotton (C) and historical paper (G) after ageing

Paper sample	The pH values of paper			
	Non treated	Treated by		
		$Ca(OH)_2$ in 2-propanol	$Mg(OH)_2$ in 2-propanol	Solution of APTES in 2-propanol
E	6.54	7.71	7.74	7.67
M	6.36	7.30	7.84	8.32
G	5.20	6.46	6.31	6.24

As it is shown in Table 1 and Table 2 the pH values of historical paper G (treated as well as non treated) are less than 7 and almost unchanged after artificial ageing. The pH values of all samples of treated paper E and C remained more than 7 after ageing.

3.2.2.2. The determination of alkaline reserve

The pH value of the paper gives no indication of amount of alkaline compounds – alkaline reserve (a. r.) – present in paper. The determination of a. r. have been performed according to standardized procedure ISO (6588-1:2005) based on titrimetry.

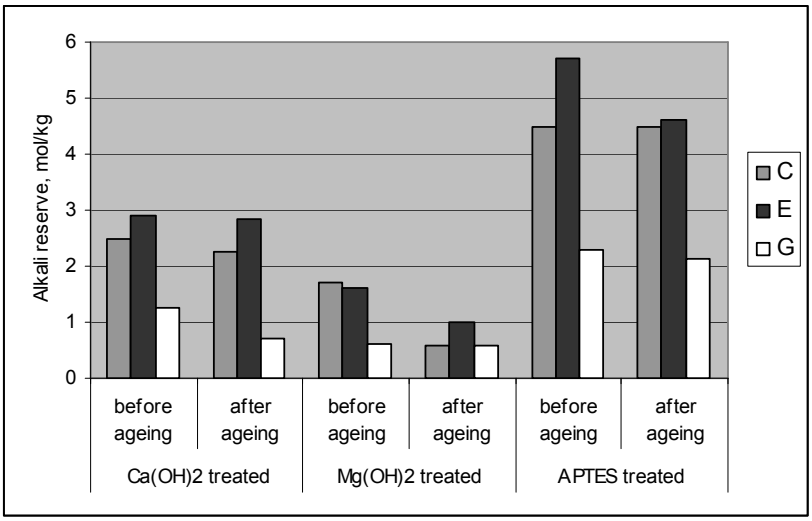


Fig. 12. The amount of alkaline reserve in different treated paper before and after thermal ageing at 105 °C for 30 days

The recommended level of alkaline reserve in permanent paper is 0.40 mol/kg. As seen in Fig. 12 required alkaline reserve is achieved in cotton and eucalyptus paper using dispersion of $Ca(OH)_2$ particles and APTES solution in 2-propanol, while with dispersion of $Mg(OH)_2$ the deacidification is less satisfactory.

3.2.2.3. The investigation of the stability of alkali treated paper by IR spectroscopy

In this part an investigation of non treated and alkali treated cotton and eucalyptus cellulose paper as well as historical paper samples before and after accelerated ageing have been performed using IR spectroscopy. The intensity of peaks at wave numbers of 1745 cm^{-1}, 1733 cm^{-1}, 1713 cm^{-1} attributed to more oxidized cellulose have been compared.

The results of IR spectroscopy (Fig. 13) revealed that paper samples treated with suspension of calcium (Fig. 13, a) or magnesium (Fig. 13, b) hydroxide particles or APTES solution (Fig. 13, c) in 2-propanol are more stable during thermal accelerated ageing for 30 days at 105 °C. Thus all three deacidification systems can prevent the degradation of cellulose. The APTES treatment showed the most effective impact in

stabilization of cellulose. Also, the hydrophobic properties of historical paper have an influence to a lesser degree of deacidification efficiency.

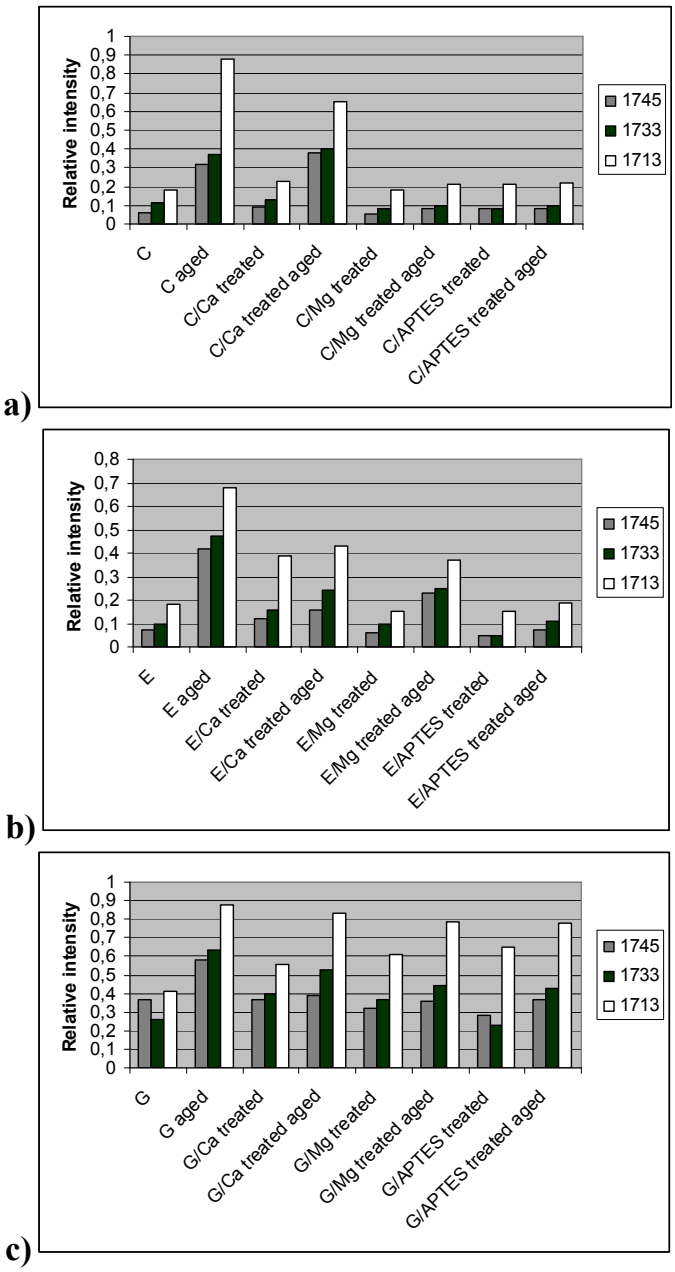


Fig. 13. The intensity of distinctive peaks of IR spectra of: a) cotton paper; b) eucalyptus cellulose paper; c) historical paper. 1745, 1733 and 1713 indicates the wave numbers, cm^{-1}

3.2.3. The investigation of surface morphology of paper by scanning electron microscopic analysis

All the cotton paper samples (treated with deacidification systems non aged and aged) were examined by scanning electron micrograph (SEM). Figure 14 shows the surface of non aged and thermal aged cotton paper samples treated with suspension of

calcium (Fig.14 a, b) or magnesium hydroxide (Fig. 14 c, d) particles, or APTES solution in 2-propanol (Fig. 14 e, f).

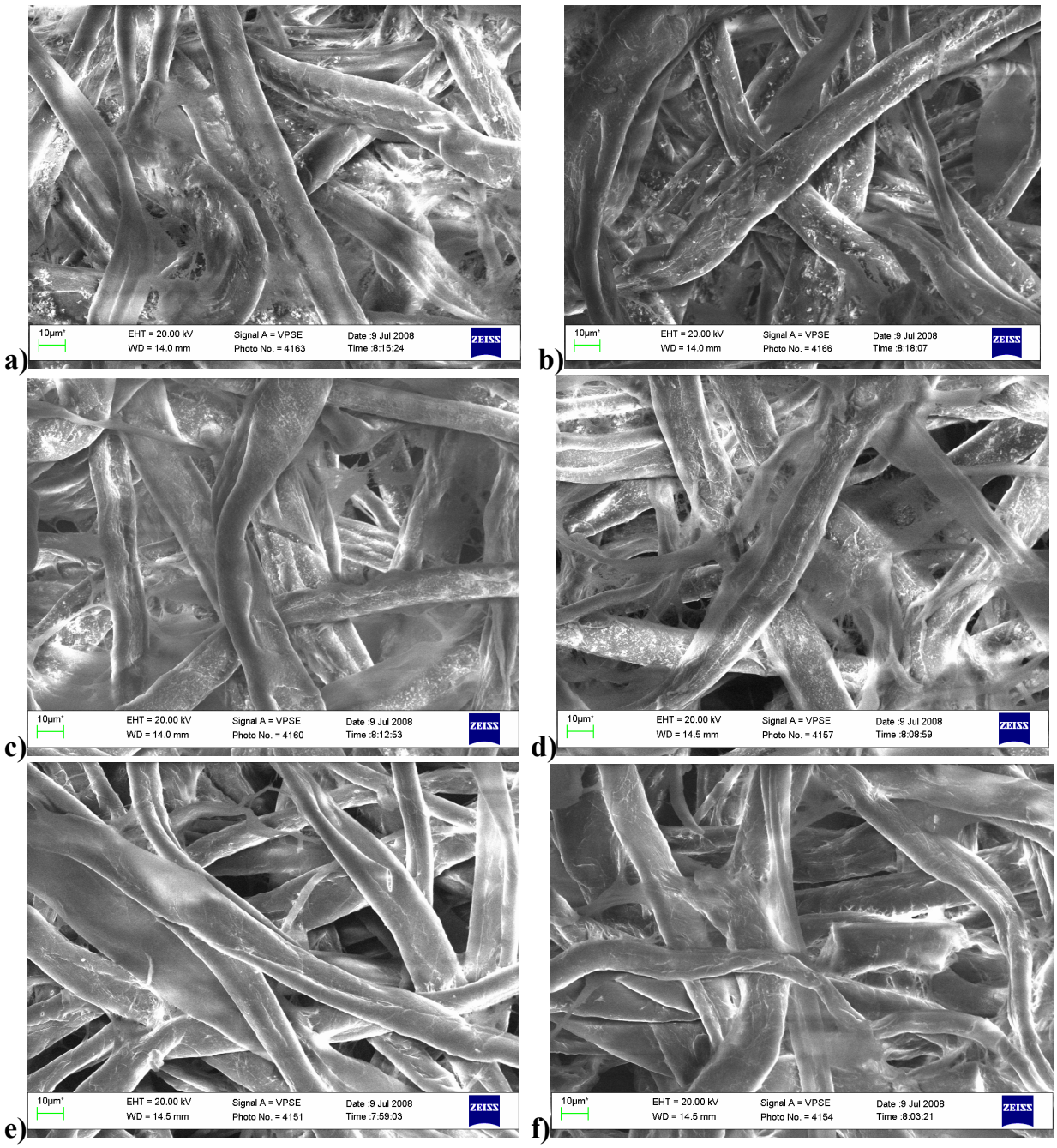


Fig. 14. Scanning electron micrographs of cotton paper (magnification 2000 X): a) treated with $Ca(OH)_2$ in 2-propanol; b) treated with $Ca(OH)_2$ and aged c) treated with $Mg(OH)_2$ in 2-propanol; d) treated with $Mg(OH)_2$ and aged; e) treated with APTES solution in 2-propanol; f) treated with APTES solution and aged (thermal ageing at 105 ^oC for 30 days have been performed)

Fig. 14 shows that calcium and magnesium hydroxide particles are adhered to paper fibres with a more homogeneous distribution. However, clustering of $Ca(OH)_2$ onto the fibers produced a white glaze or spots, while $Mg(OH)_2$ settled as “powder” on

the cellulose fibre surface. The thermal ageing (heating 30 days at 105 °C) do not lead to noticeable modification of treated fibres surface. Immersion of cotton paper in the solution of APTES in 2-propanol leads to new cross-linking network formation (Fig. 14 e). It is clearly seen in aged sample picture (Fig. 14 f), that the new poly(siloxane) polymer structure formed and after ageing tightly connected the fibres of cellulose. Thus, APTES can function as deacidification agent for the neutralization of acids and for presumptive improving the mechanical properties of paper.

3.3. The investigation of stabilization effect of new system APTES/KI and the comparison of impact of ageing conditions on the degradation of inked paper

The aim of this part of work 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. thermal ageing, thermal ageing in sealed ampoules and between glass plates (90 days at 80 °C) have been performed. For this study the sheets of paper from cotton and eucalyptus cellulose were saturated with ink 4, 5 and 8. One set of sheets were immersed into the same inks with subsequent saturation with APTES solution and KI solution in 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 aged in open vessels (90 days at 105 °C). The samples of another set were sealed in glass ampoules and aged in oven at 80 °C for 90 days. The samples of the third 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.

3.3.1. The impact of stabilization system APTES/KI on ageing resistance of inked paper

To evaluate the stabilization effect of APTES/KI the pH measurements and degree of polymerization of cellulose of treated samples were performed before and after accelerated ageing. The cold-water extraction method was used for the pH

measurements. ISO standard 5351/04 was followed for viscosity determination and for the estimation of degree of polymerization (DP). The changes in functionalities of cellulose and surface morphology of paper have been investigated as well by IR spectroscopy and SEM, AFM analysis respectively.

3.3.1.1. The determination of pH values and alkaline reserve. The investigation of surface morphology of paper

Since the cellulose degradation products formed during ageing influence the pH and consumption of the alkaline reserve the pH values and amount of alkaline compounds have been determined before and after thermal ageing. The results are presented in table 3.

Table 3. The pH values of inked (inks 4,5, 8) and non-inked cotton paper (C), eucalyptus paper (E) and inked paper with subsequent treatment by APTES/KI before and after ageing in two different ways (the pH values of inks are presented as well)

pH values of inks	Samples (paper and inked paper)	pH values before treatment with APTES/KI			pH values after APTES/KI treatment		
		Before ageing	After ageing in open vessels	After ageing in sealed ampoules	Before ageing	After ageing in open vessels	After ageing in sealed ampoules
	C	6.50	6.62	6.66	9.61	8.16	8.48
	E	6.66	6.30	6.58	9.68	8.36	8.48
1.52	4C	3.48	3.76	3.23	9.25	4.02	3.33
	4E	3.69	3.93	3.18	8.91	4.36	3.82
2.14	5C	3.64	3.88	2.92	8.96	4.21	3.74
	5E	3.77	3.72	3.18	8.45	3.92	3.51
1.62	8C	3.45	3.64	3.18	8.91	3.98	3.19
	8E	3.46	3.76	3.11	8.53	3.97	3.29

The comparison of the amount of alkaline reserve of aged and non-aged samples presented by figure 15.

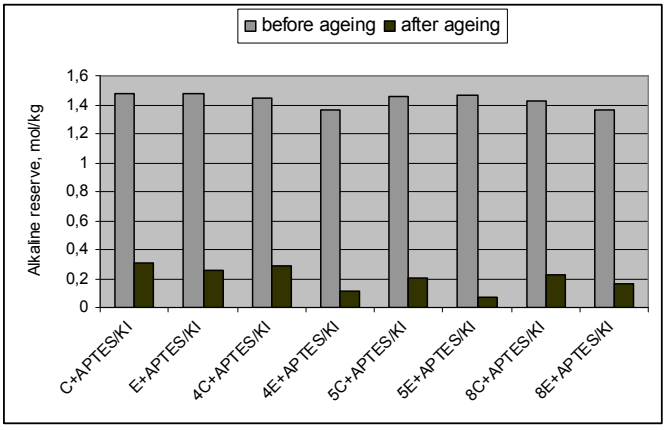


Fig. 15. The alkaline reserve of APTES/KI treated inked and non-inked cotton paper (C) and eucalyptus cellulose paper (E) before and after thermal ageing in open vessels

The alkaline reserve of all samples are less after accelerated ageing. However the consumption of alkaline compound during ageing depends on type of paper: the alkaline reserve remains larger in cotton paper than in paper from eucalyptus cellulose. It is clear from the results that the deterioration of eucalyptus cellulose passes more rapidly.

The analysis of surface morphology of paper by SEM and AFM analysis revealed that paper fibres remain not damaged and without swelling after treatment in alkaline solution (Fig. 16, 17).

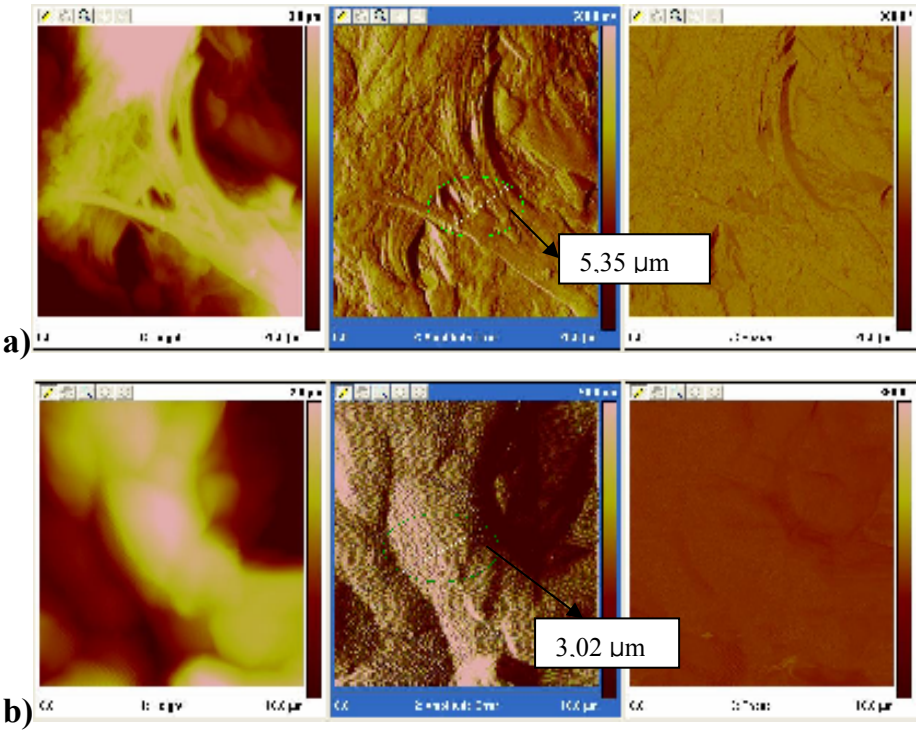


Fig. 16. AFM images of cotton paper: a) non-treated; b) treated with APTES solution in 2-propanol

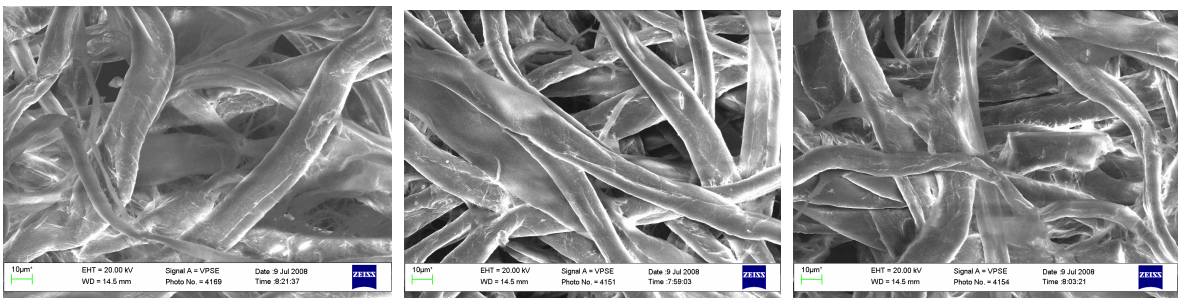


Fig. 17. Scanning electron micrographs of cotton paper (magnification 2000 X): a) virgin paper; b) treated with APTES solution in 2-propanol; c) treated with APTES solution in 2-propanol and aged for 30 days at 105 ^{o}C

3.3.1.2. The investigation of changes of polymerization degree of cellulose

Viscometric determination of DP was performed. The DP data of cotton and eucalyptus non-inked and inked samples before and after ageing in sealed ampoules and between filter paper and glass plates are shown in Figures 18, 19.

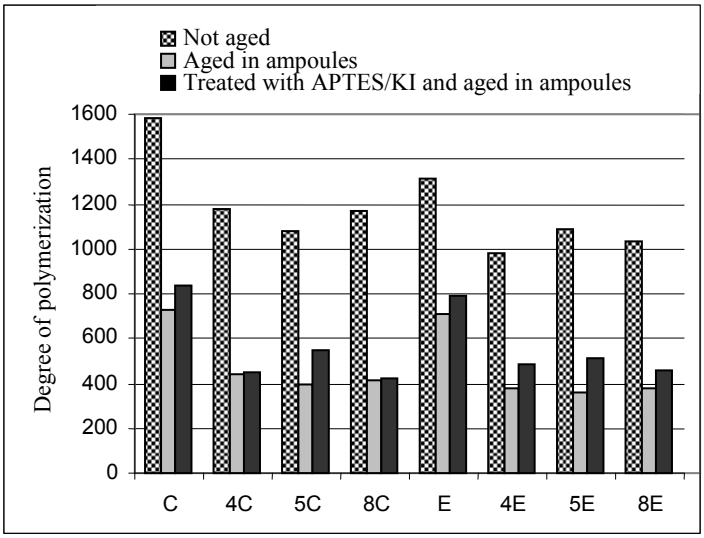


Fig. 18. DP values of cotton (C) and eucalyptus (E) paper or inked (inks 4, 5, 8) paper samples not treated and treated with APTES/KI solutions before and after ageing in sealed ampoules (at 80 °C for 90 days)

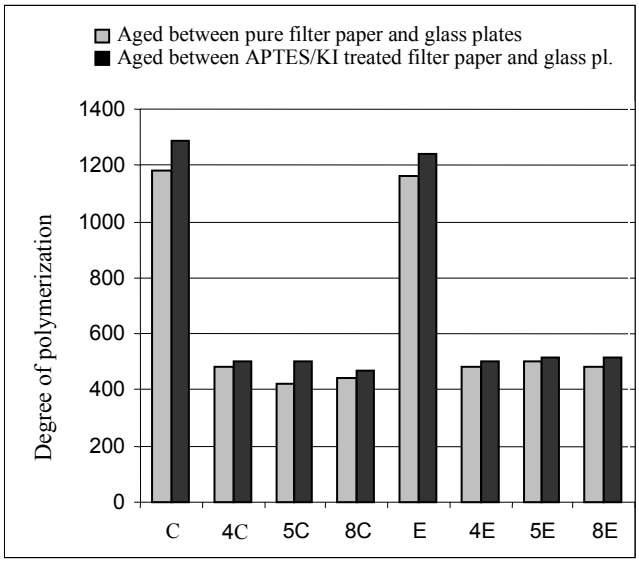


Fig. 19. The DP values of pure and inked (inks 4, 5, 8) cotton (C) and eucalyptus (E) paper samples aged at 80 °C for 90 days between glass and pure filters papers or between glass and filter papers treated with APTES/KI solution

The results presented in Fig. 18 and Fig. 19 demonstrate that the most positive impact of APTES/KI solution is for 5 ink corrosion, which contain copper (II) sulphate. Also, stabilization solution APTES/KI is capable of inhibiting degradation of non-inked

paper during ageing in ampoules and between glass and filter paper treated with APTES/KI solution. The difference of "positive behaviour" of stabilization system APTES/KI for non-inked 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 8.5–9.0), while pH of the inked samples were still low (about 3.5–4.5). The results of the experiments indicate that stabilization system APTES/KI has a positive effect when used in way of saturation of cotton and eucalyptus paper samples as well as in "passive conservation" procedure, i. e. when samples have been aged between glass plates and filter paper saturated with APTES/KI.

3.3.1.3. The investigation of effectiveness of APTES/KI by IR spectroscopy

The IR spectra of non-treated and APTES/KI treated inked and non-inked paper samples have been recorded. The intensity of peaks at wave numbers of 1749 cm^{-1}, 1733 cm^{-1}, 1716 cm^{-1}, 1684 cm^{-1}, 1662 $cm^{-1}$and 1616 cm^{-1} attributed to oxidized cellulose functional groups have been compared after accelerated ageing.

Table 4. The relative intensities of specific peaks of IR spectra of not treated and APTES/KI treated not inked and inked (ink 4, 5, 8) cotton (C) and eucalyptus (E) cellulose paper after ageing in sealed ampoules

Notation of samples	The relative intensities of specific peaks of IR spectra of paper samples at corresponding wave numbers					
	1749 cm^{-1}	1733 cm^{-1}	1716 cm^{-1}	1684 cm^{-1}	1662 cm^{-1}	1616 cm^{-1}
C	0,15	0,18	0,30	0,31	0,38	0,4
C+APTES/KI	0,06	0,09	0,13	0,28	0,45	0,44
4C	0,43	0,55	0,65	0,62	0,54	0,64
4C+APTES/KI	0,2	0,3	0,41	0,50	0,45	0,48
5C	0,44	0,6	0,74	0,63	0,49	0,7
5C+APTES/KI	0,31	0,4	0,5	0,47	0,41	0,52
8C	0,46	0,60	0,71	0,61	0,57	0,65
8C+APTES/KI	0,21	0,29	0,4	0,53	0,64	0,73
E	0,15	0,19	0,32	0,34	0,43	0,47
E+APTES/KI	0,06	0,1	0,15	0,4	0,59	0,6
4E	0,39	0,54	0,68	0,55	0,49	0,53
4E+APTES/KI	0,31	0,37	0,46	0,56	0,55	0,57
5E	0,5	0,66	0,77	0,66	0,6	0,81
5E+APTES/KI	0,38	0,49	0,62	0,55	0,47	0,58
8E	0,48	0,62	0,74	0,7	0,71	0,71
8E+APTES/KI	0,1	0,16	0,23	0,36	0,45	0,53

Decreasing of absorption intensity at listed wave numbers indicates the stabilization influence of APTES/KI system on the cellulose degradation caused by ink corrosion.

3.3.2. The investigation of the influence of APTES/KI system for the stabilization of model manuscripts

To simulate the manuscript samples line-drawings have been prepared using cotton and eucalyptus cellulose paper and inks 4, 5, 8. Model manuscripts (non-treated and APTES/KI treated) were aged in sealed ampoules as well as between filters and glass plates. The intensity of degradation has been evaluated by comparison of pH values and degree of polymerization of cellulose. The changes in color of inks have been evaluated visually.

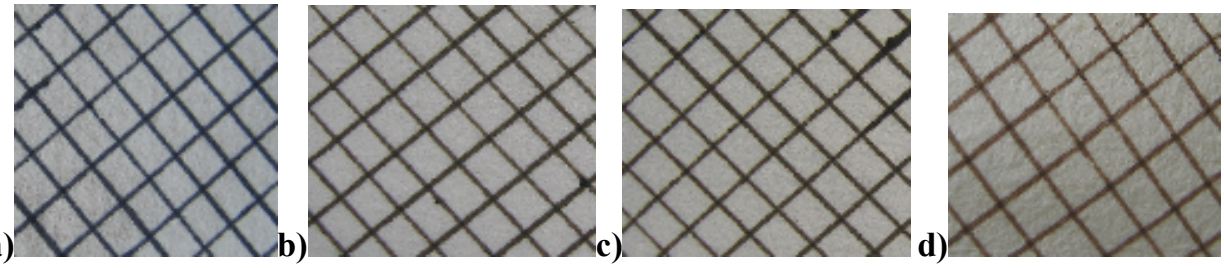


Fig. 20. The fragments of model manuscripts (cotton paper lined with ink 4): a) not aged; b) aged between pure filter paper and glass plates; c) aged between APTES/KI treated filter paper and glass plates; d) APTES/KI treated and aged in ampoule (all samples were aged at 80 °C for 90 days)

The color of paper and ink of model manuscripts has changed slightly after ageing between filter paper and glass plates. APTES/KI treated model manuscript undergoes more alteration during ageing in sealed ampoule however the ink lines remained of high intensity (Fig. 20).

3.4. The conservation of aged model and historical manuscript by stabilization system APTES/KI

The historical manuscript dated back to year 1744 and model manuscripts aged for 90 days at 80 ºC have been selected for conservation. The one half of each model manuscript and the fragment of historical manuscript with ink containing Fe(II) ions have been immersed in APTES/KI solution in 2-propanol for 10 minutes. The presence

of ink migration or color changes have been judged by appearance of samples after drying and later – after ten days.

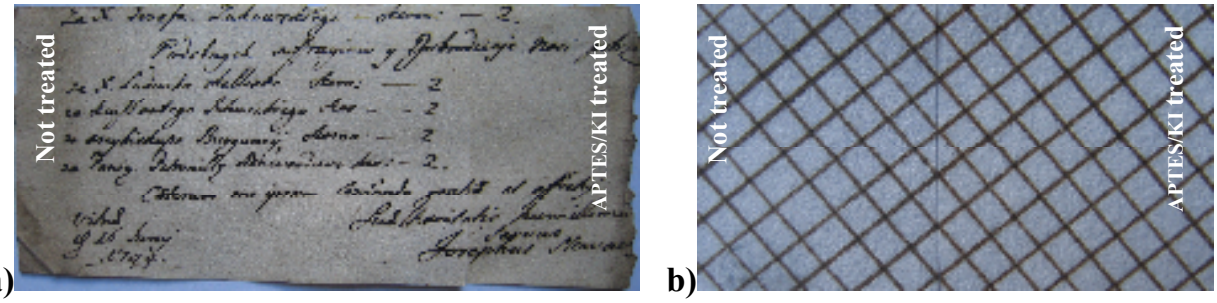


Fig. 21. The not treated and APTES/KI treated areas of: a) historical manuscript; b) model manuscript

The comparison of treated and non-treated part of samples showed no differences in color (neither ink nor paper support) (Fig. 21). The pH values of treated historical manuscript were: 6.62 before treatment with APTES/KI and 8.73 – after treatment.

CONCLUSIONS

1. All inks used in the experiment (1-8) stimulate the degradation of cotton and eucalyptus paper during artificial ageing processes. The degree of polymerization of cellulose in all inked paper samples have lessened more than in ink free paper after artificial aging. Furthermore, when inked paper was artificially aged, more oxidized functional groups occurred in these cellulose molecules.

2. The destruction of cotton and eucalyptus paper is stimulated the most when the ink with transition metal ions has been applied.

3. The intensity of paper degradation depends on the nature and the state of paper fibers. Cotton paper which consists of celluloses fibers that were less changed during the time of paper production has been more resistant to destructive factors.

4. The intensity of paper degradation depends on ageing conditions and on environment of the sample. The degradation is stimulated by thermal impact and by the impact of ultraviolet rays. Cotton fibers were more sensitive to ageing process by UV rays while the destruction of paper from eucalyptus cellulose was more rapid when the process of thermal ageing was applied.

The paper degrades less during ageing in open dishes rather than in sealed ampoules where volatile decay products could not escape from the sample.

During thermal ageing the degradation of paper is slower when paper is in alkaline environment. The degradation of samples aged between APTES/KI treated filters and glass plates happens slower than these aged between pure filter paper. Therefore, system APTES/KI is effective when used for passive conservation.

5. After deacidification of paper by the dispersions of nanoparticles of $Ca(OH)_2$ and $Mg(OH)_2$, calcium compounds are inserted into paper in larger quantities, though the alkalinity of $Mg(OH)_2$ treated paper is higher. While paper is alkalized using $Ca(OH)_2$ and $Mg(OH)_2$ nano-particles dispersion, magnesium compound alkalizes the paper more than calcium compound. Obtainable Mg compound particles are smaller and coats paper fibers more equally, however, they are inserted into paper in smaller quantities, thus, smaller alkaline reserve is obtained.

6. The procedure of alkalization of paper with APTES solution in 2-propanol meets the main requirements of paper deacidification procedures: paper soaks quickly, celluloses do not swell, the pH value of paper and alkaline reserve inserted into paper is proper.

7. The system of alkaline agent and antioxidant APTES/KI stabilizes inked paper. The process of degradation of APTES/KI treated paper samples were slower.

8. The system APTES/KI can be further investigated for stabilization of historical manuscripts with metallo-gallic inks: the paper of artificially aged model manuscripts and the fragment of historical manuscript (from year 1744) did not change its colour, ink did not fade or dispersed over the limits of characters.

The List of Original Publications by the Author

Articles in journals

1. **B. Sivakova**, O. Darčanova, A. Beganskienė, A. Kareiva. Investigation of impact of stabilization system APTES/KI on ageing resistance of inked paper. *Materials science (Medžiagotyra)*. 2009, 15 (4), 311-315.
2. **B. Sivakova**, A. Beganskienė, A. Kareiva. Investigation of damaged paper by ink corrosion. *Materials science (Medžiagotyra)*. 2008, 14 (1), 51-54.

Published contributions to academic conference

1. **B. Sivakova**, O. Darčanova, A. Beganskienė, A. Kareiva. New Antioxidants Systems for Stabilisation of Ink damaged paper. Youth in Conservation of Cultural Heritage – YOCOCU, Palermo (Italy), May 24-26th, 2010, p. 15.
2. **B. Sivakova**, V. Rubikytė, J. Blažytė, A. Beganskienė, A. Kareiva. Spectroscopic studies of damaged paper by ink corrosion. 1st Baltchem international student conference on chemistry: conference book of abstracts. Warsaw, 2008, p. 51.
3. **B. Sivakova,** O. Darčanova, A. Beganskienė, A.Kareiva. New antioxidants systems for stabilisation of ink damaged paper. In Scientific Conference of Students "Chemistry and Chemical technology" Klaipėda, 15 May, 2009. Klaipėda, 2009, p. 64-69. (Studentų mokslinė konferencija "Chemija ir cheminė technologija" Klaipėda, 2009m. gegužės 15 d. Klaipėda, 2009, p. 64-69).
4. **B. Sivakova,** O. Darčanova, A. Beganskienė, A. Kareiva. The effect of stabilization of KI/APTES solution on ink-damaged paper. Chemistry 2009: The 9-th Conference of Chemists, dedicated to 110 Anniversary of Academician Juozas Matulis. Vilnius, 2009, p. 44. (Chemija 2009: Lietuvos 9-oji chemikų konferencija, skirta akademiko Juozo Matulio 110 metų gimimo sukakčiai, Vilnius, 2009. p. 44).
5. **B. Sivakova**, O. Darčanova, A. Beganskienė, A. Kareiva. Investigation of new antioxidants systems for ink damaged paper. The Conference "Chemistry and Chemical technology" 22 - 23 April, 2009 Kaunas: Technologija, 2009. p. 20. (Konferencija "Chemija ir cheminė technologija". 2009 m. balandžio 22 - 23 d. Kaunas: Technologija, 2009. p. 20).

6. **B. Sivakova**, J. Blažytė, V. Rubikytė, A. Beganskienė, A. Kareiva. Non-aqueous deacidification methods for paper conservation. Chemistry and technology of inorganic compounds. Kaunas, 2008, p. 17. (Neorganinių junginių chemija ir technologija Kaunas, 2008, p. 17).

7. **B. Sivakova**, A. Beganskienė, A. Kareiva. Investigation of damaged paper by ink corrosion. Chemistry and technology of inorganic compounds. Kaunas, 2007.p. 14-15. (Neorganinių junginių chemija ir technologija, Konferencijos tezės. Kaunas, 2007.p. 14-15).

8. **B. Sivakova**, A. Beganskienė, A. Kareiva. Spectroscopic studies of damaged paper by ink corrosion. Chemistry 2007, The 8-th Conference of Chemists of Lithuania, Vilnius, 2007, p. 39. (Chemija 2007, Lietuvos 8-oji chemikų konferencija, Vilnius, 2007, p. 39).

9. **B. Sivakova**, J. Smirnova, A. Beganskienė. FTIR investigation of damaged paper by ink. Conference of Young Chemists of Vilnius University „Inorganic compounds: synthesis, properties and application, Burokaraistele, Varena, Lithuania, 16-17 December 2006, Neorganiniai junginiai: sintezė, savybės ir panaudojimas“, Burokaraisteles village, Lithuania, 16–17 December (2006) 40.

CURRICULUM VITAE

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1974–1979 Studies at Vilnius University, Faculty of Chemistry, Diploma in Chemistry.

Since 1983 have been working at Document restoration center of the National Library of Lithuania in different positions.

2005–2009 Post-graduate studies at the Department of General and Inorganic Chemistry, Faculty of Chemistry of Vilnius University.

2001 – 2009 lecturer at Vilnius University.

POPIERIAUS SU RAŠALU IRIMO PROCESO TYRIMAS IR NAUJŲ KONSERVAVIMO METODŲ ĮVERTINIMAS

SANTRAUKA

Rankraštinio paveldo – ypač metalo-galo rūgšties rašalu rašytų dokumentų – išsaugojimas yra labai sudėtingas uždavinys, iškylantis rinkinių saugotojams, restauravimo srityje dirbantiems mokslininkams ir praktiniu restauravimu užsiimantiems specialistams. Sunkiai sprendžiama problema yra ne tik didžiuliai irstančių dokumentų kiekiai. Norint kvalifikuotai saugoti, konservuoti ir restauruoti vertingus popierinius dokumentus, reikalingos ne tik bendros žinios apie popieriaus irimą ir jo stabilizavimą, bet ir apie rašomosios medžiagos poveikį popierinei laikmenai. Renkantis konkrečiam dokumentui tinkamą konservavimo metodą ar prognozuojant jo efektyvumo trukmę, būtina įvertinti ir atskirų rašalo komponentų poveikį.

Pagrindinis šio darbo tikslas – ištirti pagal senovinius receptus pagaminto skirtingos sudėties modelinio rašalo įtaką medvilnės ir eukalipto celiuliozės popieriaus destrukcijai bei įvertinti nevandeninių stabilizavimo sistemų efektyvumą popieriaus su rašalu stabilizavimui.

Disertaciniame darbe parodyta, kad tirtas visų rūšių modelinis rašalas skatina dirbtinio sendinimo metu vykstančią medvilnės ir eukalipto celiuliozės popieriaus destrukciją: mažėja popierių sudarančios celiuliozės polimerizacijos laipsnis, celiuliozės molekulėse atsiranda daugiau oksiduotų funkcinių grupių. Vertinant rašalo komponentų įtaką, parodyta, kad irimą labiausiai spartina rašalas, kurio sudėtyje yra pereinamųjų metalų (ypač geležies arba vario) jonų. Gauti rezultatai taip pat leido daryti išvadą, kad popieriaus irimo intensyvumas priklauso nuo popierių sudarančių plaušų prigimties ir būklės. Tirtiems destrukcijos faktoriams atsparesnis medvilnės popierius, kurį sudaranti celiuliozė yra mažiau pakitusi ruošiant plaušus popieriaus gaminimui.

Pirmą kartą palyginta skirtingų sendinimo sąlygų ir bandinio aplinkos įtaka popieriaus su rašalu irimui. Parodyta, kad, kitoms sąlygoms esant vienodoms, irimas vyksta intensyviau, kai iš bandinio aplinkos negali pasišalinti irimo produktai. Be to, destrukcija vyksta lėčiau, jei popierius yra šarminėje aplinkoje.

Popieriaus su rašalu konservavimui panaudota nauja šarminė medžiaga – 3-aminopropiltrietoksisilanas (APTES), parodyta, kad jos tirpalu 2-propanolyje galima efektyviai pašarminti medvilnės ir eukalipto celiuliozės popierių. Palyginus šarminimo šia medžiaga efektyvumą su tradicinių šarminimo medžiagų – kalcio ir magnio hidroksido – nevandeninių suspensijų poveikiu, parodyta, kad sendinimo metu APTES pašarmintas popierius rūgštėja lėčiau. Šarminant popierių APTES tirpalu 2-propanolyje, šarminimo procedūra atitinka konservavimo praktikoje keliamus reikalavimus: popierius įgirdomas greitai, jį sudaranti celiuliozė neišbrinksta, pasiekiama reikiama pašarminto popieriaus pH vertė, popieriuje sudaroma šarminės medžiagos atsarga.

Tirtas naujos šarminės medžiagos APTES ir antioksidanto KI bendras poveikis stabdant popieriaus su rašalu irimą. Parodyta, kad šarminės medžiagos su antioksidntu sistema APTES/KI 2-propanolyje stabilizuoja popierių su rašalu. Šia sistema įmirkyti bandiniai irsta lėčiau. Be to, istema APTES/KI yra efektyvi naudojant ją pasyviam konservavimui.

Atliktas sendintų modelinių rankraščių ir istorinio 1744 metų rankraščio konservavimas parodė, kad nevandeninė stabilizavimo sistema APTES/KI gali būti toliau tiriama, pritaikant istorinių rankraščių su metalo-galo rūgšties rašalu stabilizavimui: įmirkius sendintus modelinius rankraščius ir istorinio rankraščio fragmentą, popierius nepakeitė spalvos, rašalas neišbluko ir neišplito už rašmenų ribos.