

**THE TREATMENT OF ACID NEWSPRINT PAPER:
EVALUATION OF TREATMENT BY MgO OR BY
A MIXTURE OF MgO AND METHYL METHOXY
MAGNESIUM CARBONATE**

MICHAL JABLONSKÝ, SILVIA HOLÚBKOVÁ, JANA KAZÍKOVÁ, MARTINA BOTKOVÁ, ALEŠ HÁZ
SLOVAK UNIVERSITY OF TECHNOLOGY, FACULTY OF CHEMICAL AND FOOD TECHNOLOGY,
INSTITUTE OF POLYMER MATERIALS, DEPARTMENT OF CHEMICAL TECHNOLOGY OF WOOD
PULP AND PAPER
BRATISLAVA, SLOVAK REPUBLIC

MARTINA BAJZÍKOVÁ
SLOVAK NATIONAL LIBRARY, RESEARCH AND DEACIDIFICATION DEPARTMENT
MARTIN, SLOVAK REPUBLIC

(RECEIVED FEBRUARY 2012)

ABSTRACT

Degradation of cellulose is an important factor influencing its physical, mechanical, optical and chemical properties and the lifetime of paper in libraries and archival holdings. The groundwood paper made since middle of the 19th century is endangered. Documents in poor conditions need treatment which can ensure them to next generations.

To investigate the ageing stability, model groundwood newsprint paper was used. A study of the accelerated ageing of newsprint paper was performed at 98°C and 50 % RH during 0, 1, 2, 3, 5, 7, 10, 15, 20 and 30 days. The efficacy of treatment using MgO in perfluoralkanes or a mixture dispersion of MgO in perfluoralkanes and methyl methoxy magnesium carbonate in methanol (ratio 3:1) was measured and compared. This article is aimed at finding kinetic dependences for the decrease of polymerization, the decrease of folding endurance and time stability of pH value of paper undergoing accelerated ageing. Both treatments were evaluated through multifactorial evaluation system developed by Consortium KnihaSK and Library of Congress. On the basis of the multifactorial evaluation system the treatment by the MgO and by a mixture of MgO and methyl methoxymagnesium carbonate fulfilled the requirement of the Consortium KnihaSK and Library of Congress for the lifetime increase.

KEYWORDS: Deacidification, efficacy, degradation, ageing.

INTRODUCTION

Paper is relatively stable material but undergoes natural or accelerated ageing process that causes the degradation of cellulose. The degradation process relates to the presence of acid substances, moisture, light/UV radiation (Bukovský and Kuka 2001; Dufour and Havermans 2001; Rychlý et al. 2006; Robotti et al. 2007), heat/temperature (Zervos and Moropoulou 2005, 2006), oxidative agents (Kolar 1997; Havlinová et al. 2007) or microorganisms (Sinnott 1990; Ball 1997; Zerek 2006; Rakotonirainy et al. 2008). Hydrolysis and oxidation occur during the ageing process of cellulose and result in a progressive weakening of the physical strength of the paper over time (Dupont 2002). Degradation of paper is associated with the formation of low molecular product such as formic, acetic, lactic and other acids. A few studies have been committed to the analysis of the sub-products from the age degradation of paper, using gas chromatography (GC), liquid chromatography (LC) and solid-phase microextraction (SPME) coupled with GC-MS (Belardi and Pawliszyn 1989, Clark et al. 2011, Doering et al. 2000, Doering 2007, Dupont et al. 2007, Gaspar et al. 2010, Hrivnak et al. 2009a, b, Jablonský et al. 2011a, Lattuati-Derieux et al. 2004, 2006, Łojewski et al. 2010, Shahani et al. 1989, Shahani 1995, Shahani and Harrison 2002, Strlic et al. 2007, 2009, 2011, Zhang et al. 1994). The formation of these acids leads to a self-promoting hydrolytic degradation chain reaction, or auto-catalysis (Baranski et al. 2004). To prevent or minimize the lignocellulosics destruction, various deacidification processes have been developed and patented during last decades (Cedzová et al. 2006). Today, at least five true paper deacidification processes, in ten different variations are known. All the processes are based on the use of alkaline magnesium compounds (Doffey and Balzardi 2006). Deacidification using MgO-containing reagents or methyl methoxymagnesium carbonate (further MMMC) and subsequent formation of alkaline reserve have been discussed in literature (Scott 1987; Lienardy and van Damme 1990; Brandis 1994; Buchanan et al. 1994; Lienardy 1994; Porck 1996; Wächter et al. 1997; Reissland 1999; Dufour and Havermans 2001; Zumbuhl and Wuelfert 2001). Bookkeeper process is one of the most frequently applied deacidification processes used for mass deacidification of various archival documents and books. The main active substance is micronized MgO (<1 mm) dispersed in perfluoroheptane fluid (Polovka et al. 2006). The only problem consisted of a white powdery deposit on the paper and covers, especially with coated paper (Pauk 1996). MMMC is a deacidifying agent preventively used by practicioners of the Wei 'To process (Scott 1987; Lienardy and van Damme 1990; Brandis 1994; Lienardy 1994; Porck 1996; Wächter 1997; Reissland 1999; Dufour and Havermans 2001). A serious disadvantage of the Wei 'To system is the presence of methanol in deacidification solution. Certain binding media applied in writing inks and adhesives dissolve in methanol, which causes irreversible damage (bleeding of ink and print) (Porck 1996).

The decrease of the degree of polymerization straightforwardly affects all the mechanical properties (Dupont 2002; Kačík et al. 2008; Potthast 2008; Jablonský et al. 2011b). Folding endurance is the most important strength property to be affected. The great sensitivity of folding endurance in detecting the effects of ageing is regrettably counterbalanced by the low repeatability of its determination (Bansa and Ishi 1997, 1999; Zervos and Moropoulou 2006; Zervos 2010). The present work was carried out to investigate the effect of modification of paper with dispersion of MgO in perfluoroalkanes or mixture dispersion of MgO in perfluoroalkanes and MMMC in methanol during accelerated ageing at 98°C.

MATERIAL AND METODS

Accelerated ageing

Samples of paper were conditioned according to TAPPI T402 om -93 at $23 \pm 1^\circ\text{C}$, and at relative humidity of air $\text{RH} = 50 \pm 2\%$.

The samples were divided into 3 groups:

For all samples have reached equilibrium moisture content and moisture content of paper was in the range 4.1 – 5 % for the samples A, 3.7 – 4.3 % for the samples B and 3.8 – 4.9 % for the samples C.

Samples A: The samples were subsequently aged according to ISO 5630-05, using modified temperature $98 \pm 2^\circ\text{C}$ (instead of 100°C), and 50 % RH, corresponding to a paper humidity of 4.1 – 5 %. Twenty sheets of paper (A4 format) were encapsulated inside a polyethylene / aluminium / polypropylene (PET / Al / PE) composite foil (Tenofan Al/116S) by sealing off all four edges using Polystar 30D impulse tong sealer (Rische+Herfurth, Hamburg, Germany). This bag was put into another PET/Al/PE bag and completely sealed off. Batches of samples were put into the thermostat for 0, 1, 2, 3, 5, 7, 10, 15, 20 and 30 days and kept at the temperature $98 \pm 2^\circ\text{C}$ according to ASTM D 6819 – 02: Standard test method for accelerated ageing of printing and writing paper is by dry oven exposure apparatus, in which sealed glass tubes were replaced by a composite foil made of PET / Al / PE. Humidity inside the bag during accelerated ageing was $50 \pm 2\%$ and free air volume in the bag was 5 ± 1 ml. After ageing, the papers were conditioned for testing according to TAPPI T402 om – 93.

Samples B: The specimens (books with 320 sheets of paper in size A5 format) were modified by Bookkeeper dispersion of MgO at a concentration of $4.3 \text{ g}\cdot\text{dm}^{-3}$ with a particle size below $1 \mu\text{m}$ in the dispersing blend of C5-C18 perfluoralkanes and less than 0.1 % perfluorinated Mg-soap surfactant in equipment DP 7.

Samples C: The specimens (books with 320 sheets of paper in size A5 format) were modified by a mixture (3:1) Bookkeeper dispersion of MgO (3 L) and MMMC (1 L). The solution of MMMC was prepared by diluting from 10 % methanol solution of MMMC. The impregnation was carried out in equipment DP 7.

DP7: Universal laboratory modifier device that has changeable reactors with a capacity of 1, 2 and 7 litres. It is used to process modification, an exothermic polymerization processes, polymeranalog reactions in situ, impregnation cold, Rueping and other processes of impregnation with controlled distribution of impregnating substances in the cells.

The specimens (books with 320 sheets of paper in size A5 format) were modified in equipment DP7. The specimen on impregnation was fixed into a holder of the rustles, the specimen was opened and tip jet was placed in the middle book. Subsequently to evacuation of the reactor, predrying at 55°C and the pressure 0.1 MPa was carried out for 4 hours. During the evacuation, impregnation solution (4 L) was added, which circulated in the reactor for 20 minutes at the pressure 0.1 MPa. Forty paper sheets modified with MgO dispersion and dispersion of MgO and MMMC (twenty sheets of paper in size A5 format was placed of abreast) were encapsulated inside sheets of PET/Al/PE film by sealing off all four edges completely. This bag was encapsulated inside sheets of PET/Al/PE film by the sealing out all four edges completely and this procedure was repeated. The bag of samples was put into the thermostat from 0 to 30 days at $98 \pm 2^\circ\text{C}$ and $50 \pm 2\%$ RH. After ageing, the papers were conditioned for testing according to TAPPI T402 om - 93.

Folding endurance

Folding endurance (load 0.3 kg) was determined according to TAPPI T511 om – 88.

Degree of polymerization

Degree of polymerization was determined by gel permeation chromatography of tricarbanilates (Kačík and Kačíkova 2007a).

Surface pH

Surface pH was measured according TAPPI T 529 om-88 (pH of paper surface using a flat combined glass electrode). The precision in pH determinations surface pH is ± 0.2 units.

Evaluation of the treatment effectiveness

The comparison of treated / modified ($X_{t,m}$) and non-treated / unmodified ($X_{t,n}$) samples after the same period and conditions of ageing is expressed as

$$S_{t,X} = X_{t,m} / X_{t,n} \quad (1)$$

where: $S_{t,X}$ - stands for the permanence coefficient by a given treatment,
 X - the examined property (the breaking length (l_t) and the folding endurance (ω)),
 t - the ageing period.

If $S_{t,X} > 1$, the permanence is increased; if $S_{t,X} = 1$, it is not changed; $S_{t,X} < 1$, the permanence is decreased (Vrška et. al. 2004).

Linear dependence was obtained after calculating the logarithm of double folds. Time values for $\log \omega = 0$ were calculated from linear equation. Values were used for relative comparison of the efficacy of deacidification process to non-treated control sample. The lifetime of the paper terminates when logarithm of the folding endurance becomes zero ($t_{\log \omega = 0}$).

The coefficient of relative increase of the lifetime for folding endurance ($S_{t,\omega}$) is to be expressed as:

$$S_{t,\omega} = t_{\log \omega=0, m} / t_{\log \omega=0, n} \quad (2)$$

RESULTS AND DISCUSSION

The pH value is a frequently checked parameter in paper conservation research. Change of surface pH during the accelerated ageing of papers at 98°C was noticed. Fig. 1 illustrates surface pH/time plots for accelerating ageing at 98°C in unmodified and modified paper. The influence of the accelerated ageing leads to a decrease in pH with prolonged ageing for all specimens. At unmodified samples surface pH value decreases from 5.9 to 4.9 (after 30 days). The purpose of modification was to increase pH and in case of modification of samples B, it can be seen that the pH ranges from 9.3 to 6.8. As for the specimens C, surface pH, during accelerated ageing, ranges from 11.3 to 10.6. Accelerated ageing does not cause considerable decrease of pH when applying a mixture of MgO and MMMC (decreasing pH by 0.7 after 30 days of ageing). In case of modification with dispersion of MgO, a decrease of pH reached about 2.5 after 30 days. At the unmodified samples A, pH decreased by 1 after 30 days.

The continual doubt of whether to use Mg(II)-based deacidification solutions was subject of many studies (Lienardy and van Damme 1990; Kolar and Novak 1996; Bansa 1998; Strlic et al. 2005).

Bieliková (2005) found that the distribution of magnesium in paper modified using a dispersion of MgO in perfluorheptane was inhomogeneous.

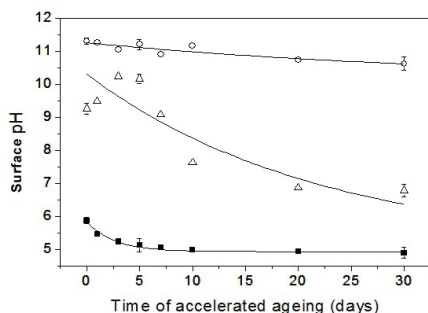


Fig. 1: Influence of accelerated ageing at 98°C on surface pH. (■) Sample A: control specimens, (Δ) sample B: deacidified sample by dispersion of MgO, (○) sample C: sample deacidified by mixture of MgO + MMMC (3:1).

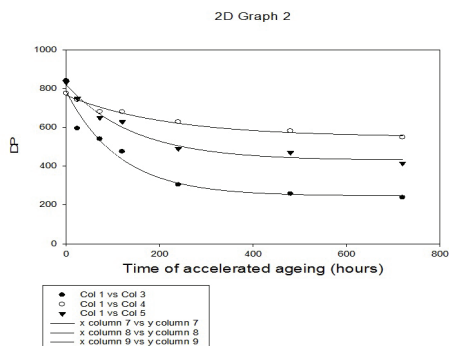
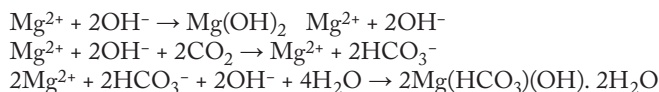


Fig. 2: Degree of polymerization change during accelerated ageing at 98°C.

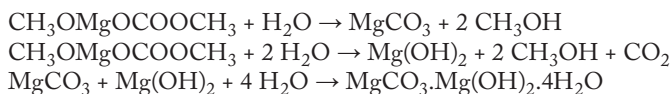
● – control sample
 ▼ – sample deacidified by dispersion of MgO
 ○ – sample deacidified by mixture of MgO + MMMC.

It was shown that MgO was present on the surface and in the pore space of paper, which are large than dispersed particles of MgO in perfluorheptane (particle sizes below 1 μm). Energy dispersive spectroscopy has proved that the magnesium ions and their compounds with the multicomponent agents and mixtures containing chemical solution with low molecular compounds (MgO and MMMC) diffuse into the paper structure more homogenously than MgO particles. The content of MgO in 1 g paper for the samples B (modified by dispersion of MgO) was 1.44 ± 0.98 mg MgO/g paper and for mixture of MgO and MMMC it was 21.11 ± 1.34 mg MgO/g paper.

It was observed that for some of the deacidification process, deacidification compounds were dispersed more homogenously on the paper surface and within the structure of paper than for others. It is generally assumed that MgO particles are transported onto the fibers of the support via capillary transport. MgO is converted to $Mg(OH)_2$ which acts as the alkaline reserve. Various possible mechanisms leading to the formation of $Mg(OH)_2$ have been proposed. In the presence of water, hydroxyl groups are formed on the surface of magnesium oxide. One of the possible mechanisms of Bookkeeper action and the formation of alkaline reserve was proposed by Zumbuhl and Wuelfert (2001):



Zumbuhl and Wuelfert (2001) showed that the dispersion agents were not only carriers for the active material but had a significant influence on deacidification and formation of an alkaline reserve. The reactions of the Bookkeeper reagent may depend strongly on the fluorinated dispersants. Zumbuhl and Wuelfert (2001) concluded that the fluorinated residues acted as retardants, slowing down the formation of $Mg(OH)_2$ and the diffusion of Mg^{2+} and OH^- ions into cellulose-bound water layers. On the other hand, in case of MMMC, this compound penetrated into the inner paper. MMMC reacts with the water in the paper and forms methanol (CH_3OH) and alkaline magnesium carbonate, a mixture of magnesium carbonate ($MgCO_3$), magnesium hydroxide ($Mg(OH)_2$) and water (Porck 1996):



The ageing process and corresponding extent of degradation are connected to changes in mechanical properties. Within the ageing process, degree of polymerization (further DP) is decreased which, in turn, (Kačík et al. 2007b, 2009) leads to a decrease in mechanical resistance of fibres, making them susceptible to shortening due to mechanical treatment (Sawoszczuk et al. 2004).

Fig. 2 represents a decrease in DP during accelerated ageing at 98°C. It is manifested that a substantial decrease (by 29.3 %) in DP occurred even during 24 hours lasting ageing when compared to the original control sample. A decrease by 71.6 % (DP = 239) was observed after 720 hours (30 days). When applying dispersion MgO as deacidification agent, a decrease in DP decelerated reaching DP = 415 following 720 hours of ageing which represents, for the time of $t = 0$, 50.2 % deceleration when compared to the deacidified sample. Treating samples with a mixture of MgO and MMMC, better results were obtained. After 30 days, DP was reduced by 29.2 %, (DP = 550), which represents a decrease by 34.6 % vs. the non-treated original sample.

Decrease in DP is associated with scission of cellulose chains. This phenomenon is clearly documented in several papers (Ekenstam 1936; Lai and Sarkanen 1967; Cosgrove et al. 1985; Nevell 1985; Guita et al. 1990; Krässig 1993; Emsley and Stevens 1994a, b; Emsley and Heywood 1995; Zou et al. 1996a, b; Emsley et al. 1997, 2000; Kolar 1997; Lai 2001; Baranski 2002; Rychlý et al. 2002; Berggren et al. 2003; Strlic et al. 2003; Baranski et al. 2005; Calvini 2005; Irklei et al. 2005). Ding and Wang (2008) introduced continuous scalar variable δ , and named it “percentage retention of DP”:

$$\delta = DP_t / DP_0 \quad (3)$$

where: DP_0 - denotes the initial degree of polymerization,
 DP_t - the real degree of polymerization, decreased as a result of deterioration due to degradation of cellulose.

At the beginning of ageing-related degradation ($t = 0$), $\delta = 1$, during degradation its value decreases, and $\delta = 0$ which means total damage of the sample.

Degradation variable of cellulose can then be defined in terms of the percentage DP loss as:

$$\omega_{DP} = 1 - \delta = 1 - DP_t / DP_0 \quad (4)$$

where: ω_{DP} - the accumulated DP loss of cellulose.

The extent of degradation can be, thus, expressed also using the above relation. At the beginning $\omega_{DP} = 0$, i.e. an average DP is preserved. $\omega_{DP} = 1$ represents a (theoretical) total damage of the sample depending on specific experimental conditions.

It is generally accepted that when DP has decreased to an average DP of about 200, the paper will lose all its mechanical strength; if $DP_0 = 1\ 000$, then $\delta = 0.2$, and the accumulated degradation critical value $\omega_{DP_{cr}} = 0.8$.

Using the Ding's and Wang's equation (2008) allows to express the course of degradation, the parameter ω_{DP}^* (see eq. 5) being the capacity of DP . Value of ω_{DP}^* can be determined introducing a limiting condition $\omega_{DP}^*(t = t_f) = 1$, where t_f is the time of degradation. At the initial

conditions $\omega_{DP}(t=0) = 0$.

$$\omega_{DP} = 1 - \delta = 1 - DP_t / DP_0 = \omega^*_{DP}(1 - e^{-k_{DP}t}) \quad (5)$$

Fig. 3 shows time dependences of ω_{DP} during accelerating ageing at 98°C for a non-treated control sample, and paper samples deacidified using an MgO dispersion or a 3:1 mixture of MgO and MMMC. As for unmodified control sample, a significant loss of DP was observed and the parameter ω^*_{DP} reached the value of 0.7 after 720 hours ageing. Contrary, for deacidified samples the values of $\omega^*_{DP}(t=720\text{ h}) = 0.5$ and $\omega^*_{DP}(t=720\text{ h}) = 0.3$ were reached when using MgO, and MgO + MMMC, respectively. The highest rate of degradation ($k_{DP} = 0.0105\text{ h}^{-1}$) was determined for the unmodified control sample. In case of the treated samples the rate constants of DP degradation are lower ($k_{DP} = 0.0073\text{ h}^{-1}$ and $k_{DP} = 0.0053\text{ h}^{-1}$) for samples treated using MgO and MgO+MMMC, respectively. The regression coefficient was in all cases $R^2 > 0.94$. This deceleration of degradation is caused by application of deacidification agents. The mechanism of their action is, however, different. Given the size of MgO microparticles, they attached on the surface of paper fibers, while liquid MMMC penetrates into the paper body.

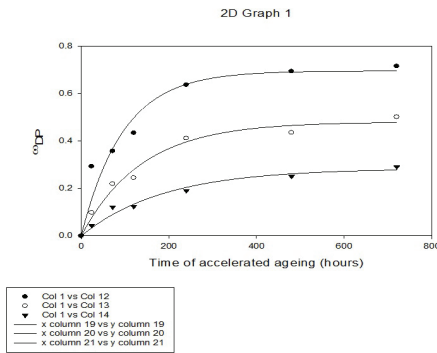


Fig. 3: Time dependence of degradation change during accelerated ageing at 98°C.

● – control sample
○ –sample deacidified by dispersion of MgO
▼ –sample deacidified by mixture of MgO + MMMC.

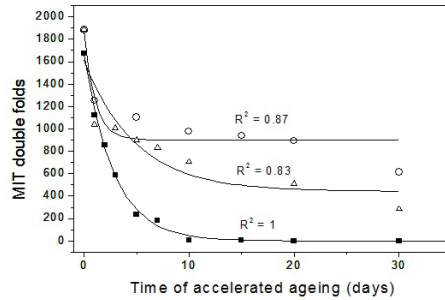


Fig. 4: Influence of accelerated ageing at temperature 98°C on the loss of folding strength (MIT double folds). (■) Sample A: control specimens, (Δ) Sample B: sample deacidified by dispersion of MgO, (○) Sample C: sample deacidified by mixture of MgO + MMMC (3 : 1).

Despite of its inaccuracy, the use of the folding endurance is widespread in the paper permanence testing, because it is very sensitive to paper ageing (Hanus 1996). It changes more rapidly during the ageing process than other mechanical or chemical properties (Browning 1977). The loss of folding strength (MIT double folds, load 0.3 kg) under accelerated ageing at 98°C for unmodified papers (sample A) and modified papers dispersion of MgO (sample B) and mixture of MgO and MMMC (sample C) (3 : 1) is shown in Fig. 4.

The regression coefficient, R^2 , approached to 1 for unmodified paper samples. At the accelerated ageing longer than 10 days, folding endurance (MD) decreased very strongly (decrease from 1672 to 8 MIT double folds). After 7 days of accelerated ageing, the loss of strength was about 89 % (187 MIT double folds after 7th day of accelerated ageing) against to unaged samples.

After 10 days of accelerated ageing we measured 8 MIT double folds and the prolonged ageing decreased the number of MIT double folds to 1. The samples ageing longer than 15 days showed small differences in comparison to those aged 10 days. For measuring the physical properties of weak papers, fold endurance is a decisive disadvantage (Shahani 1995).

Dispersion of MgO and mixture of MgO and MMMC increase of mechanical properties in modified paper against unmodified samples A. After modification by the dispersion of MgO the loss of folding endurance was 1885 in the time of accelerated ageing 0 days at 98°C. The use of modified MgO has a positive effect on the increase of the folding endurance against unmodified samples where a MIT double fold was 1672. In the case of modification by mixture of MgO and MMMC, the positive influence of application is verified (the loss of folding endurance 1884). The Fig. 3 shows that the loss of the folding endurance in the time of accelerated ageing at 98°C depends on the influence of particular modifications. In case of modifying mixture of MgO and MMMC (the regression coefficient, $R^2 = 0.87$), the lost of the decrease the folding endurance during accelerated ageing than at modified samples by dispersion of MgO (the correlation coefficient, $R^2 = 0.83$). After 30 days of accelerated ageing the increase of the loss of folding endurance at modification by dispersion of MgO (286 times against unmodified paper) after 30 days accelerated ageing occurred. Sample C (modified by mixture of MgO and MMMC) was for 30 days 2.14 times larger than at modification using dispersion of MgO.

Time value for $\log \omega = 0$ were calculated from linear equation. The coefficient of relative increase of the lifetime was calculated from formula (2). The requirement is as follows: the coefficient of lifetime prolongation $S_{v\omega}$ must reach the value of 3 as a minimum. Treatment of wood-containing paper by MgO has met this requirement $S_{v\omega} = 5.65$, which means that stability of modified paper increased by 565 %. In case of applying modified mixture of MgO and MMMC, $S_{v\omega} = 10.07$. On the basis of multifactorial evaluation system, the deacidification by the MgO and mixture of MgO and MMMC did fulfilled the Consortium Kniha SK and Library of Congress (Buchnan et al. 1994) requirements for the lifetime increase.

CONCLUSIONS

The positive effect of MgO reagents and mixture of MgO reagents and MMMC in the conservation of cellulosic materials seems to be established and is confirmed by our accelerated ageing. The results show that cellulose degradation evolution equation 5 is able to explain the cellulose protection of dispersion of MgO and mixture of the MgO and MMMC. As for unmodified control sample, a significant loss of DP was observed and the parameter ω_{DP}^* reached the value of 0.7 after 720 hours ageing. Contrary, for deacidified samples the values of $\omega_{DP}^* (t = 720 \text{ h}) = 0.5$ and $\omega_{DP}^* (t = 720 \text{ h}) = 0.3$ were reached when using MgO, and MgO + MMMC, respectively. The highest rate of degradation ($k_{DP} = 0.0105 \text{ h}^{-1}$) was determined for the unmodified control sample. In case of the treated samples the rate constants of DP degradation are lower ($k_{DP} = 0.0073 \text{ h}^{-1}$ and $k_{DP} = 0.0053 \text{ h}^{-1}$) for samples treated by MgO and MgO+MMMC, respectively. This deceleration of degradation is caused by application of deacidification agents. Dispersion of MgO and mixture of MgO and MMMC increases mechanical properties in modified paper against unmodified samples. Treatment of wood-containing paper by MgO has met this requirement reaching $S_{v\omega} = 5.65$, which means that stability of modified paper increased by 565 %. In case of samples modified by mixture of MgO and MMMC, $S_{v\omega} = 10.07$. On the basis of multifactorial evaluation system the deacidification by the MgO and mixture of MgO and MMMC did fulfilled the Consortium Kniha SK and Library of Congress (Buchnan et al. 1994) requirements for the lifetime increase.

ACKNOWLEDGMENT

We thank Project of ME SR No. 2003 c. 661/2003 Preservation, Stabilization and Conservation of Traditional Information Supports in the Slovak Republic, APVT Project No. APVT-20-034202: The deterioration of historical manuscripts and documents related to transitional elements in writing inks, APVT Project No. 0324-10 Methods of spectroscopy investigation of documents as a tool of forensic assessment and VEGA Projects No. 1/0811/11 Study of effects of exogenous factors on stability of colour layers of graphical objects of cultural heritage for its financial support. And by the project PROLIGNO : Separation and study of lignin-type substances (Grant STU for young scientist).

REFERENCES

1. Ball, L., 1997: *The hands on gardener: Composting*. Workman Publishing, New York.
2. Bansa, H., Ishi, R., 1997: The effect of different strengthening methods on different kinds of paper. *Restaurator* 18(2): 51–72.
3. Bansa, H., 1998: Aqueous deacidification - with calcium or with magnesium? *Restaurator* 19(1): 1-40.
4. Bansa, H., Ishi, R., 1999: What fibre for paper strengthening? *Restaurator* 20(3-4): 198-224.
5. Baranski, A., 2002: Ageing kinetics of cellulose and paper. *Restaurator* 23(2): 77–88.
6. Baranski, A., Dziembaj, R., Konieczna-Molenda, A., Lagan, J.M., Walas, S., 2004: On the applicability of Arrhenius equation to accelerated ageing tests. The case of alum-impregnated cellulose. *Polish Journal of Chemical Technology* 6(1): 1–8.
7. Baranski, A., Lagan, J.M., Lojewski, T., 2005: Acid-catalysed degradation. In: *Ageing and stabilisation of paper* (Eds. Strlic, M. and Kolar, J.) Ljubljana, National and University Library of Slovenia. Pp 93-109.
8. Belardi, R.P., Pawliszyn, J., 1989: The application of chemically modified fused silica fibres in the extraction of organics from water matrix samples and their rapid transfer to capillary columns. *Water Pollut. Res. J. Can.* 24(1): 179–191.
9. Berggren, R., Molin, U., Berthold, F., Lennholm, H., Lindstrom, M., 2003: Alkaline degradation of birch and spruce: Influence of degradation conditions on molecular mass distributions and fibre strength. *Carbohydrate Polymers* 51(3): 255-264.
10. Bieliková, L., 2005: Study of the distribution of substances in lignocellulosics materials on the development of multicomponent modified substances. Thesis. Bratislava: Faculty of chemical and food technology STU (in Slovak).
11. Brandis, L., 1994: Summary and evaluation of the testing sponsored by the Library of Congress of books deacidified by the FMC, AKZO and Wei To mass deacidification Processes. *Restaurator* 15(2): 109-127.
12. Browning, B.L., 1977: The application of chemical and physical tests in estimating the potential permanence of paper and papermaking materials. *Preservation of paper and textiles of historic and artistic value*. (Advances in Chemistry Series 164). Washington, D.C., American Chemical Society, Chapter 19: 275-285.
13. Buchanan, S., Bennet, W., Domach, M., 1994: An evaluation of the Bookkeeper mass deacidification process. Technical Evaluation Team, Report, Pittsburgh, Library of Congress.

14. Bukovský, V., Kuka, I., 2001: The influence of Mg on the light induced oxidation of newsprint. *Restaurator* 22(4): 208-227.
15. Calvini, P., 2005: The influence of levelling-off degree of polymerisation on the kinetics of cellulose degradation. *Cellulose* 12(4): 445-447.
16. Cedzová, M., Gallová, I., Katusčák, S., 2006: Patents for paper deacidification. *Restaurator* 27(1): 35-45.
17. Clark, A.J., Calvillo, J.L., Roosa, M.S., Green, D.B., Ganske, J.A., 2011: Degradation product emission from historic and modern books by headspace SPME/GC-MS: Evaluation of lipid oxidation and cellulose hydrolysis. *Anal. Bioanal. Chem.* 399(10): 3589-3600.
18. Cosgrove, J.D., Head, B.C., Graham, S.G., Warwicker, J.O., Lewis, T.J., 1985: A GPC study of cellulose degradation. In: *Cellulose and its derivatives* (Eds. Kennedy and Ellis). Pp 143-151, Ellis Horwood, Chichester.
19. Ding, H.Z., Wang, Z.D., 2008: On the degradation evolution equations of cellulose. *Cellulose* 15(2): 205-224.
20. Doering, T., Fischer, P., Binder, U., Liers, J., Banik, G., 2000: An approach to evaluate the condition of paper by a non-destructive analytical method. In: *Advances in printing science & technology*, 27: 27-39, *Advances in Paper and Board Performance*, 27th Research Conference of IARIGAI, (Ed. J.A. Bristow). Pira, Leatherhead.
21. Doering, T., 2007: *Altes Papier – Neue Techniken: Zerstörungsfreie Untersuchungen von Papier mit Festphasenmikroextraktion (SPME)*. BWV – Berliner Wissenschafts-Verlag, Berlin, 153 pp.
22. Doffey, M.C., Balzardi, E., 2006: Introduction. In: *Save papers! Mass deacidification Today's Experiences – Tomorrow's Perspectives*. (Eds. Blüher, A., Grossenbacher, G., Banik, G.), Swiss National Library, Bern. Pp 4-6.
23. Dufour, J., Havermans, J.B.G.A., 2001: Study of the photo-oxidation of mass-deacidified papers. *Restaurator* 22(1): 20-40.
24. Dupont, A.L., 2002: Study of the degradation of gelatin in paper upon aging using aqueous size-exclusion chromatography. *Journal of Chromatography A* 950(1-2): 113-124.
25. Dupont, A.L., Egasse, V., Morin, A., Vasseur, F., 2007: Comprehensive characterisation of cellulose- and lignocellulose degradation products in aged papers: Capillary zone electrophoresis of low-molar mass organic acids, carbohydrates, and aromatic lignin derivatives. *Carbohydrate Polymers* 68(1): 1-16.
26. Ekenstam, A., 1936: Über das Verhalten der Cellulose in Mineralsäure-Lösungen. II. Mitteil: Kinetisches Studium des Abbaus der Cellulose in Säure-Lösungen. *Berichte der Deutschen Chemischen Gesellschaft* 69(3): 553-559.
27. Emsley, A.M., Stevens, G.C., 1994a: Kinetics and mechanisms of the low-temperature degradation of cellulose. *Cellulose* 1(1): 26-56.
28. Emsley, A.M., Stevens, G.C., 1994b: Review of chemical indicators of degradation of cellulosic electrical paper insulation in oil-filled transformers. *IEE Proc. Sci. Meas. Technol.* 141(5): 324-334.
29. Emsley, A.M., Heywood, R.J., 1995: Computer modeling of the degradation of linear polymers. *Polym. Degrad. Stab.* 49(1): 145-149.
30. Emsley, A.M., Heywood, R.J., Ali, C.M.M., Eley, C.M., 1997: On the kinetics of degradation of cellulose. *Cellulose* 4(1): 1-5.
31. Emsley, A.M., Ali, M., Heywood, R.J., 2000: A size exclusion chromatography study of cellulose degradation. *Polymer* 41(24): 8513-8521.

32. Gaspar, E.M., Santana, J.C., Lopes, J.F., Diniz, M., 2010: Volatile organic compounds in paper—an approach for identification of markers in aged books. *Anal. Bioanal. Chem.* 397(1): 369–380.
33. Guita, M., Chiantore, O., Ludo, M.P., 1990: Monte-Carlo simulations of polymer degradations. 1. Degradations without volatilisation. *Macromolecules* 23(7): 2087–2092.
34. Hanus, J., 1996: Some properties of permanent paper produced in Slovakia. *Alkaline paper advocate* 9(1): 5-7.
35. Havlinová, B., Minariková, J., Hanus, J., Jancovicová, V., Szaboová, Z., 2007: The conservation of historical documents carrying iron gall ink by antioxidants. *Restaurator* 28(2): 112-128.
36. Hrivnák, J., Tolgyessy, P., Figeďyová, S., Katuščák, S., 2009a: A solid-phase microcolumn extraction method for evaluation of the condition of aged paper. *Chromatographia* 70(3-4): 619–622.
37. Hrivnák, J., Tolgyessy, P., Figeďyová, S., Katuščák, S., 2009b: Solid phase microcolumn extraction and gas chromatography–mass spectrometry identification of volatile organic compounds emitted by paper. *Talanta Journal* 80(2): 400–402.
38. Irklei, V.M., Kleiner, Y.Y., Vavrinyuk, O.S., Galbraikh, L.S., 2005: Kinetics of degradation of cellulose in basic medium. *Fibre chemistry* 37(6): 452–458.
39. Jablonský, M., Katuščák, S., Holubková, S., Hrobonová, K., Lehotay, J., 2011a: The effect of acetic and formic acid formation during accelerated ageing on embrittlement of newsprint paper. *Restaurator* 32(4): 318-347.
40. Jablonský, M., Katuščák, S., Kačík, S., Kačíková, D., 2011b: Changes in newsprint paper during accelerated ageing. *Cell. Chem. Technol.* 45(5-6): 405–411.
41. Kačík, F., Kačíková, D., 2007a: Characterization and analysis of cellulose and its derivatives. (Charakteristika a analýza celulózy a jej derivátov). *Technická univerzita vo Zvolene, Zvolen*, 93 pp (in Slovak).
42. Kačík, F., Kučerová, V., Vyboňová, E., Kirschnerová, S., 2007b: Evaluating of paper ageing by gelpermeation chromatography. (Hodnotenie starnutia papiera metódou gélovej permeačnej chromatografie). *Acta Facultatis Xylogologiae XLIX(1): 27-34* (in Slovak).
43. Kačík, F., Kačíková, D., Vacek, V. 2008: Kinetics of cellulose degradation at accelerated paper ageing. *Acta Facultatis Xylogologiae L(1): 83-90*.
44. Kačík, F., Kačíková, D., Jablonský, M., Katuščák, S., 2009: Cellulose degradation in the process of newsprint paper ageing. *Polymer Degradation and Stability* 94(9): 1509-1514.
45. Kolar, J., Novak, G., 1996: Effect of various deacidification solutions on the stability of cellulose pulps. *Restaurator* 17(1): 25-31.
46. Kolar, J., 1997: Mechanism of autoxidative degradation of cellulose. *Restaurator* 18(4): 163-176.
47. Krässig, H.A., 1993: Cellulose structure, accessibility and reactivity. *Polymer Monographs*, Vol. 11 (Ed. M.B. Huglin), Yverdon, Switzerland: Gordon and Beach Science Publishers.
48. Lai, Y.Z., Sarkanen, K.V., 1967: Kinetics of alkaline hydrolysis of glycosidic bonds in cotton cellulose. *Cell. Chem. Technol.* 1(5): 517-527.
49. Lai, Y.Z., 2001: Chemical degradation. In: *Wood and cellulosic chemistry*. (Eds. Hon, D.N.S., and Shiraishi, N.), New York, Marcel Dekker Inc.
50. Lattuati-Derieux, A., Bonnassies-Termes, S., Lavédrine, B., 2004: Identification of volatile organic compounds emitted by a naturally aged book using solid-phase micro extraction / gas chromatography/ mass spectrometry. *Journal of Chromatography A* 1026(1-2): 9–18.

51. Lattuati-Derieux, A., Bonnassies-Termes, S., Lavédrine, B., 2006: Characterisation of compounds emitted during natural and artificial ageing of a book. Use of headspace-solid-phase microextraction/gas chromatography/mass spectrometry. *J. Cult. Her.* 7(2): 123–133.
52. Lienardy, A., van Damme, P., 1990: Practical deacidification. *Restaurator* 11(1): 1-21.
53. Lienardy, A., 1994: Evaluation of seven mass deacidification treatments. *Restaurator* 15(1): 1-25.
54. Łojewski, T., Sawoszczuk, T., Łagan, J.M., Zieba, K., Baranski, A., Łojewska, J., 2010: Furfural as a marker of cellulose degradation. A quantitative approach. *Appl. Phys. A* 100(3): 873–884.
55. Nevell, T.P., 1985: Degradation of cellulose by acids, alkalis, and mechanical means. In: *Cellulose chemistry and its applications.* (Eds. Nevell, T.P and Zeronian, S.H.). Pp 225-241, Ellis Horwood.
56. Pauk, S., 1996: Bookkeeper mass deacidification process – Some effects on 20th century library material. *Abbey Newsl.* 20(4-5): 50-53.
57. Polovka, M., Polovková, J., Vizárová, K., Kirschnerová, S., Bieliková, L., Vrška, M. 2006: The application of FTIR spectroscopy on characterization of paper samples, modified by Bookkeeper process. *Vibrational Spectroscopy* 41(1): 112-117.
58. Porck, H.J., 1996: Mass deacidification: An update of possibilities and limitations. Amsterdam: European Commission on Preservation and Acces.
59. Potthast, A., Henniges, U., Banik, G., 2008: Iron gall ink-induced corrosion of cellulose: Aging, degradation and stabilization. Part 1: Model paper studies. *Cellulose* 15(6): 849-859.
60. Rakotonirainy, M.S., Dupont, A.L., Lavedrine, B., Ipert, S., Cheradame, H., 2008: Mass deacidification of papers and books: V. Fungistatic properties of papers treated with aminoalkylalkoxysilanes. *J. Cult. Her.* 9(1): 54-59.
61. Reissland, B., 1999: Ink corrosion aqueous and non-aqueous treatment of paper objects-state of the art. *Restaurator* 20(3-4): 167-180.
62. Robotti, E., Bobba, M., Panepinto, A., Marengo, E., 2007: Monitoring of the surface of paper samples exposed to UV light by ATR-FT-IR spectroscopy and use of multivariate control charts. *Anal. Bioanal. Chem.* 388(5-6): 1249-1263.
63. Rychlý, J., Strlic, M., Matisová-Rychlá, L., Kolar, J., 2002: Chemiluminescence from paper. I. Kinetic analysis of thermal oxidation of cellulose. *Polymer degradation and stability* 78(2): 357-367.
64. Rychlý, J., Matisova-Rychlá, L., Bukovský, V., Pleteniková, M., Vrška, M., 2006: The progress of ageing of lignin-containing paper induced by light and its relation to chemiluminescence – Temperature runs. *Macromolecular Symposia* 231(1): 178-192.
65. Sawoszczuk, T., Wandelt, P., Baranski, A., Lagan, J.M., Łojewski, T., Perlinska-Sipa, K., 2004: Degradation of paper as studied by fiber length measurements after hydrodynamical treatment. In: *Proceedings of the International Conference "Durability of Paper and Writing"*, Nov. 16-19, Ljubljana, Slovenia, (Eds. Kolar, J., Strlic, M., Havermans, J.B.G.A.) Pp 78-80.
66. Scott, M., 1987: Mass deacidification at the National Library of Canada. *Restaurator* 8(2-3): 94-99.
67. Shahani, C.J., Hengemihle, F.H., Weberg, N., 1989: The effect of variations in relative humidity on the ageing of paper. In: *Historic textile and paper materials. II: Conservation and characterization*, ACS Symposium Series 410, (Ed. H. Zeronian, H.L. Needles), American Chemical Society. Pp 63–79, Washington D.C..

68. Shahani, C.J., 1995: Accelerated ageing of paper: Can it really foretell the permanence of paper. *Preservation Research and Testing Series No. 9503*, Philadelphia, PA.
69. Shahani, C.J., Harrison, G., 2002: Spontaneous formation of acids in the natural aging of paper. In: *Preprints to the IIC Congress, Baltimore, Works of Art on Paper, Books, Documents and Photographs: Techniques and Conservation*, (Eds. V. Daniels, V. Donnithorne, P. Smith). Pp 189–192, London.
70. Sinnott, M.L., 1990: Catalytic mechanism of enzymic glycosyl transfer. *Chem. Rev.* 90(7): 1171–1202.
71. Strlic, M., Kocar, D., Kolar, J., Rychlý, J., Pihlar, B., 2003: Degradation of pullulans of narrow molecular weight distribution - the role of aldehydes in the oxidation of polysaccharides. *Carbohydrate Polymers* 54(2): 221–228.
72. Strlic, M., Kolar, J., Kocar, D., Rychlý, J., 2005: Thermo-oxidative degradation. In: *Ageing and stabilisation of paper*. (Ed. Strlic, M., and Kolar, J.) National and University Library, Ljubljana.
73. Strlic, M., Kralj Cigic, I., Kolar, J., de Bruin, G., Pihlar, B., 2007: Non-destructive evaluation of historical paper based on pH estimation from VOC emissions. *Sensors* 7(12): 3136–3145.
74. Strlic, M., Thomas, J., Trafela, T., Cséfalvayová, L., Kralj Cigic, I., Kolar, J., Cassar, M., 2009: Material degradomics: On the smell of old books. *Anal. Chem.* 81(20): 8617–8622.
75. Strlic, M., Kralj Cigic, I., Mozir, A., de Bruin, G., Kolar, J., Cassara, M., 2011: The effect of volatile organic compounds and hypoxia on paper degradation. *Polymer Degradation and Stability* 96(4): 608–615.
76. Vrška, M., Katusčák, S., Polovka, M., Vizárová, K., Cedzová, M., Hanus, J., Minariková, J., Bukovský, V., 2004: Lignocellulosic stabilization efficacy measurement and evaluation. *Wood Research* 49(4): 53–62.
77. Wächter, W., Liers, J., Beck, E., 1997: Paper splitting by machine at the German Library-Leipzig. *Institute of Paper Conservation (ICON) Conference Papers*. Pp 224–230.
78. Zerek, B.F., 2006: Effect of deacidification of paper objects on the device Neschen C 900 on their susceptibility to infection by selected fungi. (Wpływ odkwaszania obiektów papierowych w urządzeniu C 900 firmy Neschen na ich podatność na infekcje wybranymi gatunkami grzybów pleśniowych). *Notes Konserwatorski No. 10*: 279–288 (in Polish).
79. Zervos, S., Moropoulou, A., 2005: Cotton cellulose ageing in sealed vessels. *Kinetic model of autocatalytic depolymerization*. *Cellulose* 12(5): 485–496.
80. Zervos, S., Moropoulou, A., 2006: Methodology and criteria for the evaluation of paper conservation interventions. *Literature review*. *Restaurator* 27(4): 219–274.
81. Zervos, S., 2010: Natural and accelerated ageing of cellulose and paper: A literature review. In: *Cellulose: Structure and Properties, Derivatives and Industrial Uses*. (Eds. Lejeune, A., Deprez, T.). Pp 155–203, New York, Nova Publishing.
82. Zhang, Z., Yang, M.J., Pawliszyn, J., 1994: Solid-phase microextraction. *Anal. Chem.* 66(17): 844A–853A.
83. Zou, X., Uesaka, T., Gurnagul, N., 1996a: Prediction of paper permanence by accelerated aging. 1: Kinetic analysis of the aging process. *Cellulose* 3(4): 243–267.
84. Zou, X., Uesaka, T., Gurnagul, N., 1996b: Prediction of paper permanence by accelerated aging. Part 2: Comparison of the predictions with natural aging results. *Cellulose* 3(4): 269–279.
85. Zumbuhl, S., Wuelfert, S., 2001: Chemical aspects of the bookkeeper deacidification of cellulosic materials: The influence of surfactants. *Studies in Conservation* 46(3): 169–180.

JABLONSKÝ MICHAL, JANA KAZIKOVÁ, SILVIA HOLÚBKOVÁ, MARTINA BOTKOVÁ, ALEŠ HÁZ
SLOVAK UNIVERSITY OF TECHNOLOGY
FACULTY OF CHEMICAL AND FOOD TECHNOLOGY
DEPARTMENT OF CHEMICAL TECHNOLOGY OF WOOD, PULP AND PAPER
RADLINSKÉHO 9
812 37 BRATISLAVA
SLOVAK REPUBLIC
Corresponding author: michal.jablonsky@stuba.sk

MARTINA BAJZIKOVÁ
SLOVAK NATIONAL LIBRARY
RESEARCH AND DEACIDIFICATION DEPARTMENT
J. C. HRONSKÉHO 1
036 01 MARTIN
SLOVAK REPUBLIC