

KINETIC DEPENDENCES FOR THE DECREASE OF POLYMERIZATION OF PAPER UNDERGOING ACCELERATED AGEING

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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. Groundwood paper made around the middle of the 19th century is endangered. Documents in poor condition need treatment to prolong their lifespan for the use of future 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 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 investigated. This paper aims at finding kinetic dependences for the degree of polymerization (further DP) decrease and time stability of pH value of paper undergoing accelerated ageing. The highest rate of degradation ($k_{DP} = 0.0105 \pm 0.0023 \text{ h}^{-1}$) was determined for the unmodified control sample. In the case of the treated samples, the rate constants of DP degradation were lower ($k_{DP} = 0.0073 \pm 0.0010 \text{ h}^{-1}$ and $k_{DP} = 0.0053 \pm 0.0009 \text{ h}^{-1}$) for samples treated by MgO and MgO+MMMC, respectively.

Keywords: deacidification, efficacy, degradation, ageing

INTRODUCTION

Paper is a relatively stable material, but it undergoes natural or accelerated ageing, which causes the degradation of cellulose. The degradation process relates to the presence of acid substances, moisture, light/UV radiation,^{1,4} heat/temperature,^{5,6} oxidative agents^{7,8} or microorganisms.⁹⁻¹² 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.¹³ Degradation of paper is associated with the formation of low molecular products, such as formic, acetic, lactic and other acids. The formation of these acids leads to a self-promoting hydrolytic degradation chain reaction, or auto-catalysis.¹⁴ To prevent or minimize the destruction of lignocellulosics, various deacidification processes have been developed and patented in the last few decades.¹⁵ Today, at least five paper deacidification processes, in ten different variations are known. All the processes are based on the use of alkaline

magnesium compounds.¹⁶ Deacidification using MgO-containing reagents or methyl methoxymagnesium carbonate (further MMMC) and subsequent formation of alkaline reserve have been discussed in literature.^{2,17-25} 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.²⁶ The only problem consists in a white powdery deposit on the paper and covers, especially on coated paper.²⁷ MMMC is a deacidifying agent preventively used by practitioners of the Wei-To process.^{2,17-24} A serious disadvantage of the Wei To system is the presence of methanol in the deacidification solution. Certain binding media applied in writing inks and adhesives dissolve in methanol, which causes irreversible damage (bleeding of ink and print).²²

The decrease of the polymerization degree straightforwardly affects all the mechanical properties.^{13,28,29}

A large number of mathematical models, hypotheses and theories for cellulose degradation can be found in literature.³⁰⁻⁴¹ The first kinetic model of cellulose deterioration has been proposed by Ekenstam.³⁰ Next, Hill and his colleagues³⁶ proposed a similar model with an additional equation that describes the behavior of another degradation process by zero-order kinetics. These models have been extended to describe the behavior of cellulose deterioration under varying physical conditions as reported in a number of studies.^{14,35,37,38,42-44}

The present work has been carried out to investigate the effect of the treatment with a dispersion of MgO in perfluoralkanes or a mixture dispersion of MgO in perfluoralkanes and MMMC in methanol on the polymerization degree of paper during accelerated ageing at 98 °C.

In this paper, the process of deacidification has been examined on original and treated samples. Deacidification is evaluated from the difference in polymerization degree of cellulose between two samples. The polymerization degree is further estimated using different models, describing the evolution of cellulose deterioration. Note that the latest contribution of Ding and Wang⁴⁴ was previously considered.

EXPERIMENTAL

Experimental samples/materials

Commercial groundwood newsprint paper (grammage – 45 g/m², aqueous pH = 4.5-5.0), containing mechanically bleached groundwood (55%), bleached sulphite pulp (20%), recycled fibers (15%) and kaolin (10%), was used in all experiments.

Accelerated ageing and preparation of samples

Paper samples were conditioned for 24 hours at $T = 23 \pm 1$ °C, RH = 50 ± 2%.

The samples from all tested deacidification processes were subsequently aged according to ISO/DIS 5630-5, using modified temperature 98 ± 2 °C (instead of 100 °C), and 50% RH, corresponding to a paper humidity of 4-5%.

The samples were divided into 3 groups:

Samples A: Twenty sheets of paper (A4 format) were encapsulated inside a PET/Al/PE composite foil (Tenofan Al/116S) by sealing off all four edges, using Polystar 30D impulse tong sealer (Rische+Herfurth, Hamburg, Germany). The bag was put into another PET/Al/PE bag and was completely sealed off. The

bag with the samples was put into the thermostat for 0, 1, 2, 3, 5, 7, 10, 15, 20, 30 and 60 days at 98 ± 2 °C.

Samples B: The specimens (books with 320 sheets of paper of A5 format) were modified by Bookkeeper dispersion of MgO at a concentration of 4.3 g/dm³, with a particle size below 1 µm, in the dispersing blend of C5-C18 perfluoralkanes and less than 0.1% perfluorinated Mg-soap surfactant in a DP 7 equipment.

Samples C: The specimens (books with 320 sheets of paper of 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 a 10% methanol solution of MMMC. The impregnation was carried out in a DP 7 equipment.

On impregnation, the specimen was fixed to a holder, opened and a tip jet was placed in the middle of the book. Subsequently to the evacuation of the reactor, predrying was carried out at 55 °C and a pressure of 0.1 MPa for 4 hours. During the evacuation, an impregnation solution (4 L) was added and was circulated in the reactor for 20 minutes at a pressure of 0.1 MPa. Twenty paper sheets modified with Bookkeeper dispersion and dispersion Bookkeeper+MMMC. The modified sheets were encapsulated in PET/Al/PE film and all four edges were completely sealed off. The bag was re-encapsulated in sheets of PET/Al/PE film twice, all four edges being completely sealed off and then it was thermostated from 0 to 30 days at 98 ± 2 °C.

Degree of polymerization

The degree of polymerization was determined by gel permeation chromatography of tricarbonylates (CTC).⁴⁵ All GPC results represent the mean of two different samples, and each CTC was chromatographed twice (total of four runs for each sample).

Surface pH

Surface pH was measured according to TAPPI T 529 om-88 (pH of paper surface using a flat combined glass electrode). The precision in pH determinations was surface pH $\leq \pm 0.02$ units.

RESULTS AND DISCUSSION

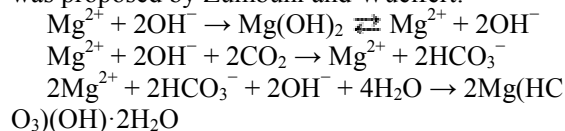
The pH value is a frequently investigated parameter in paper conservation research. A change in surface pH during the accelerated ageing of papers at 98 °C was noticed. Fig. 1 illustrates surface pH/time plots for accelerated ageing at 98 °C in unmodified and modified paper. The influence of the accelerated ageing led to a decrease in pH with prolonged ageing for all specimens. For unmodified samples, surface pH value decreased from 5.9 to 4.9 (after 720 hours). The purpose of the modification was to increase pH and, in the case of samples B, it can be noted

that the pH ranged from 9.3 to 6.8. As for specimens C, during accelerated ageing, their surface pH ranged from 11.3 to 10.6. Accelerated ageing did not cause considerable decrease of pH, when applying a mixture of Bookkeeper and MMMC (pH decreased by 0.7 after 720 hours of ageing). In the case of the modification with the Bookkeeper dispersion, a decrease of pH of about 2.5 was reached after 720 hours. For unmodified samples A, pH decreased by 1 after 720 hours.

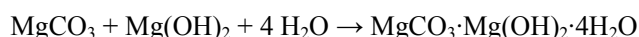
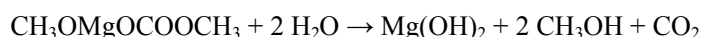
The use of Mg(II)-based deacidification solutions was the subject of many studies.^{18,46-48} Bielikova⁴⁹ found that the distribution of magnesium in paper modified by a dispersion of MgO in perfluorheptane was inhomogeneous. It was shown that MgO was present on the surface and in the pores of paper, which are larger than the MgO particles dispersed in perfluorheptane (particle sizes below 1 μm). Energy dispersive spectroscopy proved that the magnesium ions and its compounds with the multicomponent agents and mixtures containing chemical solution with low molecular compounds (MgO and MMMC) diffuse into the paper structure more homogeneously than MgO particles. For samples B (modified by a Bookkeeper dispersion), the content of MgO in 1 g paper was 1.44 ± 0.98 mg MgO/g paper and for samples C (modified by a mixture of Bookkeeper and MMMC), it was 21.11 ± 1.34 mg MgO/g paper.

It was observed that, for some of the deacidification processes, deacidification

compounds were dispersed more homogeneously on the paper surface and within the structure of paper than for others. It is generally assumed that MgO particles are transported onto the fibres of the support via capillary transport. MgO is converted to $\text{Mg}(\text{OH})_2$, which acts as an alkaline reserve. 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 the alkaline reserve was proposed by Zumbuhl and Wuelfert:²⁵



Zumbuhl and Wuelfert²⁵ showed that the dispersion agents were not only carriers for the active material, but had a significant impact on deacidification and on the formation of the alkaline reserve. The reactions of the Bookkeeper reagent may depend strongly on the fluorinated dispersants. Zumbuhl and Wuelfert²⁵ concluded that the fluorinated residues acted as retardants, slowing down the formation of $\text{Mg}(\text{OH})_2$ and the diffusion of Mg^{2+} and OH^- ions into cellulose-bound water layers. On the other hand, MMMC penetrated the inner paper, reacted with the water in the paper and formed methanol (CH_3OH) and alkaline magnesium carbonate, a mixture of magnesium carbonate (MgCO_3), magnesium hydroxide ($\text{Mg}(\text{OH})_2$) and water.²²



The ageing process and corresponding extent of degradation involve changes in mechanical properties. During the ageing process, the DP decreases, which, in turn,^{50,51} leads to a decrease in the mechanical resistance of fibres, making them susceptible to shortening due to mechanical treatment.⁵²

Fig. 2 represents a decrease in DP during accelerated ageing at 98 °C. It may be noted that a substantial decrease in DP (by 29.3%) occurred even during 24 hours of ageing, compared to the original control sample. A decrease by 71.6% (DP = 239) was observed after 720 hours (30 days). The application of an MgO dispersion as deacidification agent slowed down the process of

degradation. After 720 hours of artificial ageing, DP was 415, which represents a decrease of DP of about 50.2%, compared to the sample deacidified by MgO in time $t = 0$ h. By 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.

The decrease in DP is associated with the scission of cellulose chains, a phenomenon that is well documented in a number of papers.^{7,30-35,37-41,53-62} Ding and Wang⁴⁴ introduced the continuous scalar variable δ , and named it "percentage retention of DP":

$$\delta = DP_t / DP_0 \quad (1)$$

where DP_0 denotes the initial degree of polymerization and DP_t – the real degree of

polymerization, decreased as a result of deterioration due to degradation of cellulose.

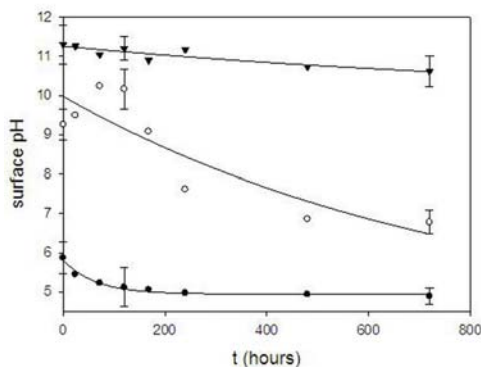


Figure 1: Influence of accelerated ageing at 98 °C on surface pH; ● – control sample; ○ – sample deacidified by MgO dispersion; ▼ – sample deacidified by MgO+MMMC mixture

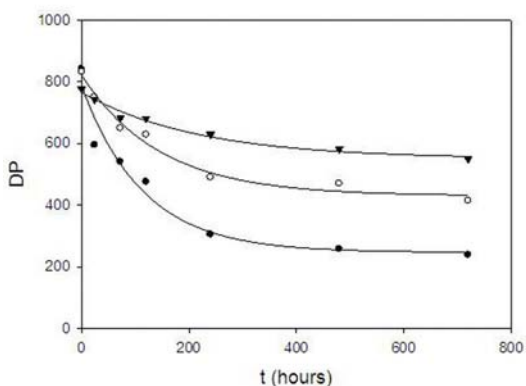


Figure 2: Variation of polymerization degree during accelerated ageing at 98 °C; ● – control sample; ○ – sample deacidified by MgO dispersion; ▼ – sample deacidified by MgO+MMMC mixture

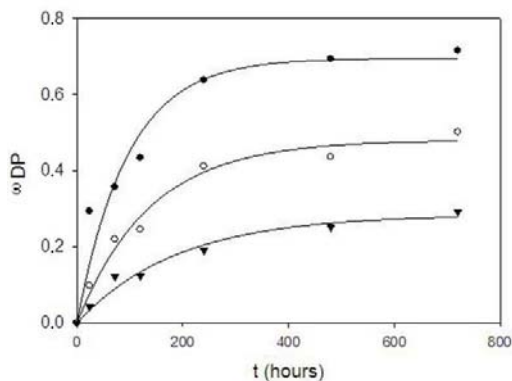


Figure 3: Time dependence of accumulated cellulose polymerization degree loss (ω_{DP}) during accelerated ageing at 98 °C; ● – control sample; ○ – sample deacidified by MgO dispersion; ▼ – sample deacidified by MgO+MMMC mixture

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.

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

$$\omega_{DP} = 1 - \delta = 1 - DP_t/DP_0 \quad (2)$$

where ω_{DP} is the accumulated DP loss of cellulose.

The extent of degradation can be, thus, also expressed 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 decreases to an average DP of about 200, the

paper loses all its mechanical strength; if $DP_0 = 1000$, then $\delta = 0.2$, and the accumulated degradation critical value $\omega_{DPcr} = 0.8$.

Using Ding and Wang's equation⁴⁴ allows to express the course of degradation, the parameter ω_{DP}^* (see Eq. 3) being the capacity of DP. The 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. Under the initial conditions $\omega_{DP}(t = 0) = 0$.

$$\omega_{DP} = 1 - \delta = 1 - DP_t/DP_0 = \omega_{DP}^*(1 - e^{-kDP \cdot t}) \quad (3)$$

Fig. 3 shows time dependences of ω_{DP} during accelerated ageing at 98 °C for a non-treated control sample, and for paper samples deacidified by the MgO dispersion or the 3:1 mixture of MgO and MMMC. As for the unmodified control sample, a significant loss of DP was observed and

the parameter ω^*_{DP} reached the value of 0.70 ± 0.05 after 720 h ageing. On the contrary, for deacidified samples, the values of $\omega^*_{DP}(t = 720 \text{ h}) = 0.48 \pm 0.02$ and $\omega^*_{DP}(t = 720 \text{ h}) = 0.28 \pm 0.02$ were reached when using MgO, and MgO+MMMC, respectively. The highest rate of degradation ($k_{DP} = 0.0105 \pm 0.0023 \text{ h}^{-1}$) was determined for the unmodified control sample. In the case of the treated samples, the rate constants of DP degradation were lower ($k_{DP} = 0.0073 \pm 0.0010 \text{ h}^{-1}$ and $k_{DP} = 0.0053 \pm 0.0009 \text{ h}^{-1}$) for the samples treated by MgO and MgO+MMMC, respectively. The regression coefficient was in all cases $R^2 > 0.94$. This deceleration of degradation was caused by the application of deacidification agents. The mechanism of their action was, however, different. Given the size of MgO microparticles, they attached onto the surface of paper fibers, while the MMMC liquid penetrated into the paper body.

CONCLUSION

The positive effect of MgO reagents and of the MgO reagents and MMMC mixture in the conservation of cellulosic materials seems to have been established and has been confirmed by accelerated ageing. The results show that cellulose degradation evolution Equation 3 can explain cellulose protection by the MgO dispersion and the MgO and MMMC mixture. As for the unmodified control sample, a significant loss of DP was observed and the parameter ω^*_{DP} reached the value of 0.70 ± 0.05 after 720 hours of ageing. On the contrary, for deacidified samples, values of $\omega^*_{DP}(t = 720 \text{ h}) = 0.48 \pm 0.02$ and $\omega^*_{DP}(t = 720 \text{ h}) = 0.28 \pm 0.02$ were reached, when using MgO, and MgO+MMMC, respectively. The highest rate of degradation ($k_{DP} = 0.0105 \pm 0.0023 \text{ h}^{-1}$) was determined for the unmodified control sample. In the case of the treated samples, the rate constants of DP degradation were lower ($k_{DP} = 0.0073 \pm 0.0010 \text{ h}^{-1}$ and $k_{DP} = 0.0053 \pm 0.0009 \text{ h}^{-1}$ for the samples treated by MgO and MgO+MMMC, respectively). This deceleration of degradation was caused by the application of deacidification agents.

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