

## KINETIC STUDY OF ARTEFACT PAPER DEGRADATION. ASSESSMENT OF DEACIDIFICATION EFFECTS BY FOLDING ENDURANCE

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The present study investigates the stabilization of a 60 year old paper artefact *via* deacidification. Paper sheets originating from a naturally-aged artefact book were subjected to accelerated ageing performed at 98 °C during 0, 3, 5, 10 and 15 days. A set of samples were deacidified before being subjected to accelerated aging. Deacidification was performed using magnesium ethoxide and titanium ethoxide (METE) dissolved in hexamethyldisiloxane (HMDO) and the properties of the thus treated samples were measured and compared to control samples. This study aims at finding kinetic dependences for the decrease in the degree of polymerization and folding endurance of the paper subjected to accelerated ageing. The deacidification effects were evaluated by the folding endurance of the paper artefact through the multifactorial evaluation system developed by Consortium Kniha<sup>SK</sup> and Library of Congress.

**Keywords:** deacidification, kinetic description of degradation

### INTRODUCTION

The deteriorative effect of paper acidity has been known for many years. Naturally occurring degradation of paper at normal temperature is so slow that its symptoms can be observed only after several years. Considering the fact that natural degradation of paper is such a time-consuming process, in order to study the degradation effects on paper, as well as possible ways to prevent them, it became necessary to use artificial ageing tests. These tests are standardized, consisting in accelerating the changes in paper properties, and are usually carried out at elevated temperature. Accelerated ageing tests are used to elucidate the mechanism and rate of degradation, as well as to evaluate the effects of long-lasting protection practices, including paper deacidification.

Upon ageing, the mechanical properties of the paper are worsening and it becomes brittle. For this reason, many paper-based artefacts are in such poor condition that it is almost impossible to use them and their handling requires careful

attention. The deterioration of paper properties is determined by the degradation of the cellulose, hemicellulose and lignin macromolecules, caused by ageing, which leads to an increase in the proportion of the low molecular weight fraction and a decrease in the mean degree of polymerization. The adverse consequences of ageing are also manifested by the deterioration of optical properties.

The degradation mechanism and kinetics of lignocellulose-based paper supports are not yet clarified in detail. Moreover, there are several conflicting opinions on this topic and new knowledge in this area can bring progress in paper stabilization and protection. Also, nowadays, several approaches and functions are used to describe the degradation kinetics, but these are insufficient and/or inadequate. The main problem is that when correlating the concentration of fracturing units and the degree of polymerization results, frequent errors emerge, mainly because of

using various measurement units. In addition, some misleading interpretations have been adopted that normally lack the necessary consistency needed to establish a systematic order in the available information. A critical analysis of the available literature shows that the application of chemical kinetics principles to issues of cellulose degradation is still in its infancy.

The folding endurance parameter monitored during accelerated ageing procedures is related to the extent of oxidative and hydrolytic damage to cellulosic fibers.<sup>1</sup> Previously, folding endurance was suggested as a suitable indicator of paper deterioration caused by natural or accelerated ageing.<sup>2,3</sup> On the other hand, the measurement of folding endurance is coupled with lower precision, as well as the necessity of precise conditioning during experiments.<sup>2</sup> Almost all of the objective evaluation studies have focused on the heat-induced ageing stability and efficacy of mechanically perfect paper.<sup>4,6</sup> The effects of deacidification of old or pre-aged paper and documents have been investigated in several studies,<sup>7-10</sup> but a systematic comparative evaluation of deacidification processes has not been carried out on old paper or paper documents.

At present, deacidification procedures are applied on non-aged papers.<sup>4,5,11-16</sup> Commonly, model samples of new acidic paper are used for investigation. The properties of degraded (aged) and new (non-aged) papers differ substantially. Aged paper is more brittle, less resistant to mechanical stress and the cellulose in its composition has a lower degree of polymerization. It has been proved experimentally that the same deacidification technology applied to aged and non-aged papers leads to different results in the evaluation of efficacy.<sup>16</sup> It means that a preservation system that has been proved effective for model samples of acidic groundwood paper need not be favourable for real degraded materials.

In this paper, the process of deacidification has been examined on sheets from a genuine artefact book. The polymerization degree was estimated using different models, describing the evolution of cellulose deterioration.

## EXPERIMENTAL

### Paper samples

Sheets from a genuine book ("A Szabadság Árnýékában", by Aczél Tamás, published in 1953), stored in the Slovak National Library (SNL) in Martin, were used as paper samples. The paper sheet samples

had a basis weight of 70 g/m<sup>2</sup>, a surface pH of 4.5-5, and a Kappa number of 28.1. The samples were divided into two sets to allow comparison: 5 samples were artificially aged for 0, 3, 5, 10 or 15 days, and were used as control samples, denoted as "non-treated"; another 5 samples were first deacidified as described below and then aged for 0, 3, 5, 10 or 15 days.

### Deacidification

The deacidification procedure was carried out by a process protected by patent SK287845.<sup>17</sup> The samples were first pre-dried, *i.e.* the normal moisture content of 5% was reduced to <0.5% by heating at 105 °C for 72 hours. The drying was subsequently followed by deacidification. The chamber was completely flooded with the deacidification solution, consisting of 10% magnesium ethoxide and titanium ethoxide (METE) dissolved in hexamethyldisiloxane (HMDO). After the solution was drained, the samples were vacuum dried in order to remove the solvent. Subsequently, the samples were exposed to humidity. The paper regained its previous moisture content and deacidification reactions took place, during which alcohol was released. The paper samples were conditioned according to TAPPI T402 om-93<sup>18</sup> at 23 ± 1 °C, and relative humidity RH = 50 ± 2%. The samples were subsequently aged (0, 3, 5, 10 and 15 days) and kept at 98 ± 2 °C according to ASTM D 6819-02,<sup>19</sup> where the sealed glass tubes were replaced by a composite foil made of polyethylene/aluminium/polypropylene (Tenofan Al/116S). During accelerated ageing, the humidity inside the bag was 50 ± 2% and free air volume in the bag was 5 ± 1 ml. After ageing, the paper samples were conditioned for testing according to TAPPI T402 om-93.

### Degree of polymerization

The degree of polymerization, DP, was determined by gel permeation chromatography (GPC) of cellulose tricarbanilates (CTC).<sup>20,21</sup> All GPC results represent the mean of two different samples, and each CTC was chromatographed twice (total of four runs for each sample).

### Folding endurance

Folding endurance (load 0.3 kg) was determined according to TAPPI T511 om-88.<sup>22</sup>

### Evaluation of deacidification efficacy

The comparison of deacidified ( $X_{t,m}$ ) and non-deacidified ( $X_{t,n}$ ) samples after ageing for the same period of time and under the same conditions is expressed as:

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

where  $S_{t,X}$  stands for the permanence coefficient of a given treatment, X is the examined property (breaking

length ( $l_t$ ) and folding endurance ( $\omega$ ),  $t$  is the ageing period.

If  $S_{t,x} > 1$ , the permanence is increased; for  $S_{t,x} = 1$ , it is not changed;  $S_{t,x} < 1$ , the permanence is decreased.<sup>23</sup>

Time values for  $\log \omega = 0$  were calculated from the linear equation. The values were used for relative comparison of the efficacy of the deacidification process with regard to non-treated control samples. The lifetime of a paper terminates when the logarithm of folding endurance becomes zero ( $t_{\log \omega = 0}$ )

The coefficient of the relative increase in folding endurance ( $S_{t,\omega}$ ) is expressed as:<sup>23,24</sup>

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

## RESULTS AND DISCUSSION

Samples of naturally aged acidic groundwood paper originating from an artefact book were analysed to evaluate the deacidification efficacy by determining the mechanical properties of paper. Figure 1 illustrates the dependence of folding endurance ( $\omega$ , -) on ageing time ( $t$ , days) at 98 °C. For the control non-aged sample, the folding endurance reached 227. During accelerated ageing at 98 °C, the folding endurance rapidly decreased and the number of double folds decreased to only 1 after 10 days of ageing. It means that the paper strength decreased by 99.6%.

Following the treatment by the 10% solution of magnesium-titanium ethanolate, the decrease in the double fold number was reached in time  $t = 0$ ,

however, during the process of ageing, the stabilizing effect of the deacidification system was observed. Thus, because of the deacidification treatment, the folding endurance of the unaged sample decreased to 155 double folds. During accelerated ageing, the folding resistance further decreased, but at a slower pace than in the case of the non-deacidified samples, reaching 31 double folds after 15 days of ageing. After 10 days, the folding endurance of the treated sample reached  $42 \pm 23$ . This indicates the favourable influence of the deacidification treatment. To assess the folding endurance,  $S_{t,\omega}$ , the  $\omega$  values were transformed to  $\log \omega$  and  $S_{t,\omega}$  was calculated.

The coefficients of linear dependence derived from the data in Figure 1 are tabulated in Table 1. Subsequently, the factor of folding endurance,  $S_{t,\omega}$ , was calculated with regard to the untreated control sample. The multicriterial evaluation developed by Kniha<sup>SK</sup> and Library of Congress stipulates that an endurance factor higher than 3 is satisfactory. In our investigation, the paper sample subjected to the deacidification process presented folding endurance  $S_{t,\omega} = 4.0$ . Considering the results obtained, it can be concluded that the samples subjected to the treatment by the 10% impregnation solution of HMDO+METE preserve their properties 4.0 times longer than untreated samples.

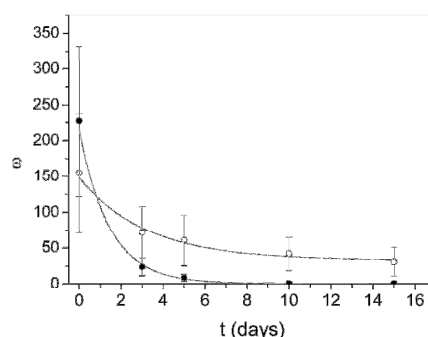


Figure 1: Influence of accelerated ageing at a temperature of 98 °C on the loss of folding strength (MIT double folds); ● control sample; ○ deacidified sample

Table 1

Parameters of equation  $\log \omega = A + B \cdot t_{(\log \omega = 0)}$ , for control and deacidified samples, and the coefficient of relative increase in folding endurance ( $S_{t,\omega}$ )

Sample	A (-)	B (days <sup>-1</sup> )	$t_{(\log \omega = 0)}$ (days)	$S_{t,\omega}$
Deacidified sample	1.7595	-0.0349	50.5	4.0
Control	1.9027	-0.1507	12.6	1

According to Zou *et al.*,<sup>25</sup> the loss of fibre brittleness is, in turn, due to depolymerisation of the cellulose caused by acid-catalysed hydrolysis. Acid hydrolysis causes chain scission of cellulose macromolecules, generating carbohydrate fragments. These fragments are oxidised to carboxylic acids, and cause the autocatalytic degradation of paper. The addition of Mg alkaline reserve has an effect on the degradation mechanism. In conservation studies, it is important to realise that, by reducing the carbonyls, we may greatly reduce the rate of degradation. The removal of carbonyl groups, from which enediols are formed, contributes to the stabilisation of paper.<sup>26</sup>

Cellulose as a polymer sometimes shows a deviating performance from classic polymer behaviour. The decrease in DP is associated with scission of cellulose chains. This phenomenon is clearly documented in several papers.<sup>12,27-41</sup> To describe the kinetics of cellulose degradation, the Ekenstam equation is mostly used:<sup>27,30</sup>

$$\ln(1-1/DP_0) - \ln(1-1/DP_t) = kt \quad (3)$$

According to the description of cellulose hydrolysis by the Ekenstam equation, the error increases for zero- or first order kinetic modelling (Eq. 4).<sup>30</sup>

In the event that  $DP_0$  and  $DP_t$  reach high levels, this equation can be simplified to the form:

$$SFCU = 1/DP_t - 1/DP_0 = kt \quad (4)$$

where SFCU represents the ratio of broken glucose units to the total glucose units of a cellulose chain.

Meanwhile, for heterogeneous systems, Equation 4 can be adjusted to the following form:

$$1/DP_t - 1/DP_0 = \alpha kt \quad (5)$$

Equation 5 has been widely used to describe various types of cellulose degradation, such as acidic degradation, light ageing, dry or moist thermal ageing in ovens.<sup>25,32</sup>

Emsley *et al.*<sup>34</sup> argue that the reaction rate in Equation 2 should not be a constant, because it decreases during the ageing process. In order to correct this deviation, Emsley *et al.*<sup>35</sup> proposed a modified Ekenstam equation (Eq. 6).

$$1/DP_t - 1/DP_0 = k_{10}/k_2(1 - e^{-k_2 t}) \quad (6)$$

where  $k_{10}$  and  $k_2$  are constants.

Also, the measured data for DP are better described by Equation 6.

Ding and Wang<sup>39,40</sup> used the time-temperature superposition method<sup>40</sup> and the percentage of DP

loss as a measure for anticipating the degree of degradation.<sup>39</sup> There is still an ongoing discussion on how to properly treat kinetic data and how to correctly model the processes.<sup>41</sup>

The DP is a frequently checked parameter in paper conservation research. The mechanical, chemical and technical properties, as well as the stability of the cellulose properties, depend primarily on the molecular weight of the cellulose and molecular weight distribution (MWD). The molecular weight of polymers is most easily measured and expressed by weight average molecular weight ( $M_w$ ), mostly characteristic of higher molecular fractions, and by number average molecular weight, as estimated directly by osmometry and other methods based on the number of molecules ( $M_n$ ). The other specific averages, as estimated directly using the centrifugation methods ( $M_z$ ,  $M_{z+1}$ ), could be used for better understanding the solution and other properties. Suitable parameters for the complex distribution of solution properties are polydispersity parameters.<sup>20,21</sup> To measure these cellulose parameters by gel permeation chromatography (GPC), it is necessary to dissolve it. However, cellulose is not easily soluble in common solvents without degradation. The selection of an appropriate solvent system will depend on the preferred method for analysis.

From a theoretical point of view, the number-averaged degree of polymerization ( $DP_n$ ) that can be calculated from  $M_n$  should be applicable. However, comparisons between  $M_n$  determined by light scattering and viscosity data have shown that such correlations are weak, whereas the weight-averaged molar mass  $M_w$ , despite the included weighting factor, correlated better to the viscosity data. Another limitation to applying the Ekenstam equation is that it requires the sample under consideration to be a linear, monodispersed polymer of high molar mass.<sup>30</sup> This does not apply to pulps that contain celluloses and hemicelluloses with polydispersity indices of up to 10. In this work, the DP was calculated by the  $M_w$  parameter.

The mean DP for the non-aged control sample was 1257 and, after 15 days of ageing, it decreased by 51.1%. Following deacidification by METE in HMDO, the initial DP of the non-aged sample was 1150, while after 15 days of ageing, it decreased only by 11.8%. It is clear evidence that, by applying the deacidification mixture, a significant inhibition of the degradation processes

was obtained. The evolution of the mean DP as a function of the ageing time is illustrated in Figure 2.

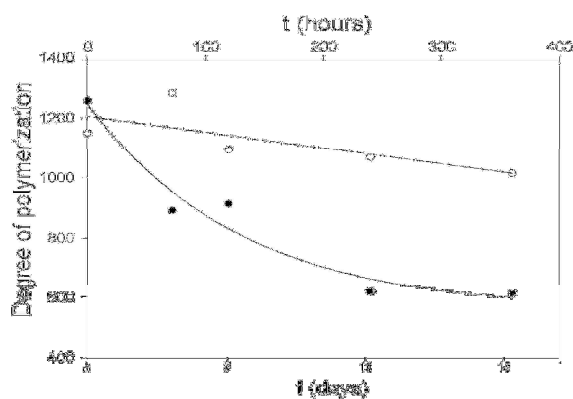


Figure 2: Variation of polymerization degree during accelerated ageing at 98 °C; ● control sample; ○ deacidified sample

Figure 3 exhibits the ratio of cleaved to total number of bonds in cellulosic chains as a function of ageing time at 98 °C.

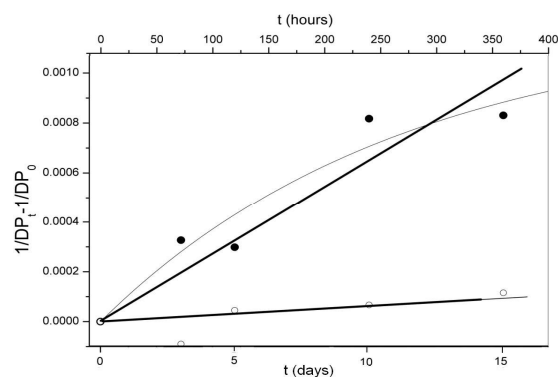


Figure 3: Ratio of cleaved to total number of bonds in cellulosic chains as a function of ageing time at 98 °C; ● control sample; ○ deacidified sample; — curve fitting by Equation 6; - - curve fitting by Equation 4

Table 2  
Parameters calculated from Equations 4 and 6, data in Figure 3

Sample	Eq. 4		Eq. 6		
	$k$ (hours <sup>-1</sup> )	$R^2$	$k_{10}$ (hours <sup>-1</sup> )	$k_2$ (hours <sup>-1</sup> )	$R^2$
Control	$2.68 \times 10^{-6}$	0.871	$4.44 \times 10^{-6}$	$3.7 \times 10^{-3}$	0.934
Deacidified sample	$2.74 \times 10^{-7}$	0.483	$2.74 \times 10^{-7}$	$5.68 \times 10^{-8}$	0.483

For the untreated sample, this ratio is  $8.3 \times 10^{-4}$  after an ageing time of 15 days. Due to deacidification, the ratio dropped to  $1.16 \times 10^{-4}$ . The values of the parameters estimated for individual curves are listed in Table 2. Equation 4 is not, however, optimal to describe degradation due to accelerated ageing. Equation 6 seems to be more suitable to express the degradation kinetics of the untreated samples. As for the deacidified samples, the regression coefficient value is identical for both equations.

## CONCLUSION

The present study has demonstrated that paper treatment using a hexamethyldisiloxane (HMDO) solution of magnesium-titanium ethoxide (METE) leads to slowing down the degradation process of paper subjected to accelerated ageing. The efficacy of the modification was evaluated by the folding endurance parameter in accordance with the multifactorial system developed by Kniha<sup>SK</sup> and the Library of Congress. The folding endurance parameter reached the value of 4.0 for treated and artificially aged paper, thus satisfying

the requirement stipulated for the multifactorial evaluation system (required value >3). In the experiments, paper sheets from a genuine artefact book were modified by METE in HMDO and they showed 3.7 times higher stability than the untreated samples. The investigation of degradation due to ageing by determining the mean degree of polymerization (DP) revealed that the applied modification induced a substantial inhibition of the degradation process of cellulose. After 15 days of accelerated ageing at 98 °C, the decrease in DP represented just 11.8% versus 51.5%, shown by the control sample. To describe the degradation kinetics, two standard equations expressing the evolution of degradation reactions were applied. It has been established that the reduction of the ratio of cleaved bonds to the total number of units in cellulosic chains (CSFU) occurring in untreated samples during accelerated ageing at 98 °C is better described using the equation  $CSFU = 1/DP_t - 1/DP_0 = k_{10}/k_2(1 - e^{-k_2t})$ , compared to  $1/DP_t - 1/DP_0 = kt$ . In the case of the modified samples, the regression coefficient ( $R^2 = 0.483$ ) is identical for both equations.

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