CELLULOSE CHEMISTRY AND TECHNOLOGY

FORMATION OF ACETIC AND FORMIC ACID IN UNMODIFIED AND MODIFIED PAPERS DURING ACCELARATED AGEING

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Organic acids are spontaneously generated in significant concentrations during natural ageing of all cellulose-based papers, the alkaline ones included. The present study reviews the paper degradation research devoted to the identification and determination of the role of light products formed during paper ageing. Accelerated ageing was performed at 98 °C and 50% RH, for 60 days. The main objective of the present study was to investigate the influence of the Mg cations included in the alkaline reserve on the progress of degradation during accelerated ageing of paper. The changes in the ratio of acetic/formic acids and the role of Mg^{2+} ions during accelerated ageing – in the investigated unmodified and modified papers – with dispersion of MgO or MgO and MMMC (methyl methoxy magnesium carbonate) mixture are discussed. The obtained results show that, during accelerated ageing, acetic and formic acids are produced in both unmodified and modified papers. The higher content of Mg^{2+} ions in modified paper increases the formation of acetic and formic acids more than in unmodified paper. The reason for this behaviour might be the strong promoting role played by the Mg^{2+} ions in the formation of the mentioned organic acids.

Keywords: acetic acid, formic acid, degradation, Mg^{2+} ions

INTRODUCTION

Paper degradation is an inevitable process,[1] related to the presence of acid substances, moisture, light/UV radiation,[2-5] heat/ temperature,[6,7] oxidative agents[8-11] or microorganisms.[12-14] It has been shown that deterioration of the mechanical properties of paper through ageing is caused by the presence of acids in the sheet.[15-17] In time, hydrolysis[18-21] and oxidation,[18-23] occurring during cellulose ageing, result in a progressive weakening of the physical strength of paper.[24] The influence of the oxidation process leads to the formation and release of the degradation products containing a carbonyl group (C=O) and the double bond (C=C).[25-26] Paper degradation is associated with the formation of low molecular products, such as formic, acetic, lactic acids and others. Several researchers have pointed out the important role played by acidic degradation products (VOCs) in paper ageing and several analytical methods have been developed for the extraction and determination of volatile compounds.[27-45] Other analytical techniques applied, including gas (GC) and liquid chromatography (LC), have identified a few low molecular weight acids, namely acetic, propionic and levulinic acids.[46] It has been reported that the regression between them and other cellulose and hemicellulose degradation products, as well as the paper strength parameters, have been evaluated by multivariation data analyses.[47]

In the USA, the National Institute for Standards and Technology completed a preliminary study concerning the identification of degradation products both in the presence and absence of sulphur dioxide.[48] It has been shown that several organic acids (formic, acetic, lactic acids) are spontaneously generated in significant concentrations during the natural ageing of all cellulose-based papers, including alkaline papers containing alkaline fillers. Easily detectable concentrations of formic, acetic, lactic, glycolic, oxalic and a few other unidentified acids accumulate within a few months, following the manufacture of paper stored under ambient conditions.[49] Earlier works showed that acidic degradation products tend to accumulate inside polyester encapsulations and other enclosures, thereby speeding up paper ageing.[50,51]

The fact that acidic degradation products are produced during accelerated ageing of acidic paper in a humid environment was clearly established at NBS in the seventies.[52] However, these data did not discuss the accumulation of these acids within a paper mass, such as a book, and the subsequent autocatalytic nature of the degradation process. Bigourdan and co-workers[53] reported that the capacity of paper loaded with an alkaline reserve to neutralize the exposure to acetic acid was not directly correlated to its initial concentration. A significant amount of absorbed acetic acid can coexist with the residual alkaline reserve in the paper structure.

To stop degradation and save the millions of books stored in archives, different technologies of deacidification and fibre strengthening were invented, and considerable efforts have been devoted to finding new additives, such as scavengers of the free radicals, natural and synthetic compounds, inorganic compounds, solvent and improved original technologies of deacidification.[54-56] The present work investigates the formation of acetic and formic acids and their molar ratio, in unmodified and modified paper, with dispersion of MgO or MgO and MMMC (methyl methoxy magnesium carbonate) mixture, during accelerated ageing at 98 °C and 50% RH.

EXPERIMENTAL

Raw material

Commercial wood-containing newsprint paper (grammage: 45 g/m, pH determined by cold extraction: 4.5-5.0), containing mechanically bleached groundwood (55%), bleached sulphite pulp (20%), recycled fibres (15%) and clay (10%) was used in all experiments.

The newsprint paper used in the experiments was directly made per order, based on the requirements of the Project "Preservation, stabilization and conservation of the traditional information supports in the Slovak Republic" (Kniha^{SK}). This type of paper has a selected composition, to reflect the paper quality of the most endangered books in a library of the Slovak Republic, in terms of pH and content of the mechanically bleached groundwood pulp.

Accelerated ageing at 98 °C

The paper samples were conditioned according to TAPPI T402 om-93 at 23 ± 1 °C, and relative air humidity, RH = 50 ± 2%. The samples were divided into 3 groups. All samples reached equilibrium moisture content, the paper moisture content ranging between 4.1-5% for samples A, 3.7-4.3% for samples B and 3.8-4.9% for samples C.

Samples A: The samples were subsequently aged according to ISO 5630-05, at a modified temperature of 98 ±2 °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 a Polystar 30D impulse tong sealer (Rische&Herfurth, Hamburg, Germany). The bag was put into another PET/Al/PE bag and completely sealed off. Batches of samples were put into the thermostate for 0, 1, 2, 3, 5, 7, 10, 15, 20, 30 and 60 days and kept at 98 ± 2 °C, according to ASTM D 6819-02: Standard test method for accelerated ageing of printing and writing paper, by means of a dry oven exposure apparatus, in which the sealed glass tubes were replaced by a composite foil made of PET/Al/PE. Humidity inside the bag during accelerated ageing was of 50 ± 2%, and the free air volume in the bag was of 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, A5 format) were modified by Bookkeeper dispersion of MgO, at a concentration of 4.3 g/dm^3 (particle size below 1 μm in the dispersing blend of C5-C18 perfluoralkanes and below 0.1% perfluorinated Mg-soap surfactant in equipment DP 7).

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

A DP7 universal laboratory modifier device with changeable reactors and a capacity of 1, 2 and 7 L was used for process modification, for exothermic polymerization processes, *in situ* polymer analogous reactions, cold impregnation, Rueping and other impregnation processes with controlled distribution of the impregnating substances in the cells.

The specimens (books with 320 sheets of paper, A5 format) were modified in equipment DP7. The specimen for impregnation was fixed into a holder of the rustles, then opened, a tip jet being placed in the middle of the book. After evacuation of the reactor, predrying at 55 °C, at a pressure 0.1 MPa was carried out for 4 h. During evacuation, an impregnation solution (4 L) was added and circulated in the reactor for 20 min, at a pressure of 0.1 MPa. Forty paper sheets modified with MgO and, respectively, MgO and

MMMC dispersion (twenty sheets of paper, A5 format being placed abreast) were encapsulated inside the sheets of the PET/Al/PE film by sealing off completely all four edges. The bag was encapsulated inside the sheets of the PET/Al/PE film by completely sealing out all four edges, the procedure being repeated. The bag of samples was thermostated from 0 to 30 days at 98 ± 2 °C and 50 ± 2% RH. After ageing, the papers were conditioned for testing, according to TAPPI T402 om -93.

High-performance ion-exchange chromatography

Materials

Sulphuric acid and acid standards (acetic and formic acids) of highly pure grades were purchased from Merck. The water used in the eluent was purified by a Millipore Elix 5 system.

Sample preparation

Approximately 2 g of paper were accurately weighed and 15 mL of pure water (resistivity at 25 °C > 5 MΩ.cm, TOC <30 μg/L) were added. The mixture was mixed for 2 h and subsequently filtered through a 0.45 μm filter, and 20 μL of filtrate were injected into the analytical column.

Instruments and conditions

The used HPLC system consisted of a DeltaChrom SDS 030 isocratic pump, a 7125 Rheodyne injector with a 20 μL injection loop, a thermostate Model LCT 5100, a Knauer variable wavelength detector (set at 210 nm), and a CSW32 software for peak identification and integration. Chromatographic separations of acids were performed with a Polymer IEX H-form column (250 x 8 mm I.D., 8 μm). The mobile phase included 9 mmol/L sulphuric acid. The column temperature was set at 20 °C and the flow rate of the mobile phase was of 0.8 mL/min.

Identification and quantification

Formic and acetic acids were detected spectrophotometrically at 210 nm. The retention times were of 9.7 ± 0.2 min and 10.7 ± 0.1 min for formic and acetic acids, respectively. The identification of acids in the water extract of paper was based on the comparison of their retention factors (formic acid k = 1.21 ± 0.03, acetic acid k = 1.44 ± 0.03).

Calibration curves were constructed by performing a regression linear analysis of the peak area *versus* the concentration of the acids. Based on a four-point calibration, a linear response (R = 0.99) was observed from the limit of determination to 20 mg/mL of the studied acids.

The detection limits were of 10.7 μg/mL for formic acid and of 18.4 μg/mL, respectively, for acetic acid, while the determination limits were of 42.8 μg/mL for formic acid and 92.2 μg/mL for acetic acid, respectively.

Cold extract pH

Cold extract pH was measured according to TAPPI T 509 om-02 (cold extraction, 1 g samples per 70 mL of water, 1 h). The precision in the pH determinations of the cold extract is estimated to be <± 0.2 units.

MIT double folds

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

RESULTS AND DISCUSSION

Figure 1 illustrates the cold extract pH/time for accelerating ageing at 98 °C and 50% RH, in unmodified and modified paper. The influence of accelerated ageing leads to a decrease of pH with prolonged ageing of all specimens. In unmodified samples, the value of cold extract pH decreased from 6.65 to 5.24 (after 30 days). The effect of modification was to increase pH – when the B samples were modified by MgO, the pH ranged from 9.21 to 5.24. In cold extract C specimens, during accelerated ageing, pH ranged from 10.43 to 10.07. The influence of accelerated ageing on pH decrease does not reach a considerable value at accelerated ageing with modification by a mixture of MgO and MMMC (a decrease of 0.36 in pH after 30 days of ageing). In the case of the modification with the dispersion of MgO, after 30 days, pH decreased by about 3.97. In the unmodified A samples, the pH decrease was of 1.59 after 30 days.

The continual doubt on whether to use Mg^{2+}-based deacidification solution was the subject of many studies.[57-60] From the above considerations, two effects can be taken into consideration, namely: the effect of a higher solubility of $MgCO_3$, inducing higher pH values of $MgCO_3$-containing papers, and the effect of the cation.[61]

Bielikova[62] found out that the distribution of magnesium in paper modified using a MgO dispersion in perfluoroheptane was inhomogeneous. It was shown that MgO was present on the surface and in the paper pores, which are larger than the dispersed particles of MgO in perfluorheptane (particle sizes below 1 μm). Energy dispersive spectroscopy has shown that the magnesium ions and their compounds with multicomponent agents and mixtures containing a chemical solution with low molecular compounds (MgO and MMMC) diffuse into the paper structure more homogenously than the MgO particles.

Consequently, the insufficiency of the dispersed MgO particles present in paper may be less effective on the removal of carboxylic acids.[63-64]

Table 1 lists the concentration of formic and acetic acids as a function of time in accelerated ageing for the samples of studied papers, modified by two processes in the DP 7 equipment. For samples B, the content of MgO in 1 g paper was of 1.44 ± 0.98 mg MgO/g paper, while for the MgO and MMMC mixture, it was of 21.11 ± 1.34 mg MgO/g paper. On the basis of this evaluation of the contents of carboxylic acids (formic and acetic acids), an unambiguous increase in the concentration of acetic acid during accelerated ageing and a moderate increase of formic acid for unmodified specimens (sample A) may be seen.

In the modified samples (subjected to both modifications), an increase in the content of carboxylic acids was observed, comparatively with samples A. This increase is evidently higher for the samples submitted to ageing with the modification by the MgO and MMMC mixture. Let us assume that this increase in the contents of carboxylic acids was due to a higher amount of MgO present in paper, than in the case of the modification with the MgO and MMMC mixture, but thereby these compounds of magnesium are, in the case of the MgO and MMMC mixture, dispersed homogenously on the paper surface and within the paper structure. The effect of magnesium or of its compounds on paper degradation was confirmed by several authors.[65-68] The conclusion to be drawn is that magnesium or compounds containing magnesium have a catalytic effect on the formation of carboxylic acids (Table 1).

Figure 2 illustrates the effect of accelerated ageing on the acetic/formic acids ratio for unmodified specimens (samples A), as well as for the specimens modified by the dispersion of MgO (samples B) and of the MgO-MMMC mixture (samples C). On the basis of carboxylic acids ratio, it can be seen, that during accelerated ageing, in unmodified samples with prolonged ageing, the concentration ratio of acetic acid to formic acid increases. After 30 days, the acetic/formic acids ratio was of 3.98, the value recorded after 60 days being of 5.52. For both modifications, the effect of the modification processes on the change in the ratio of carboxylic acids during accelerated ageing at 98 °C and 50% RH can be observed. It was found that when the dispersion of MgO was applied, the acetic acid to formic acid ratio varied between 1.75-3.83. In case of the 30-day accelerated ageing, the ratio of carboxylic acids was of 2.29. In the samples modified by the MgO and MMMC mixture (samples C), a decrease in the ratio of carboxylic acids can be seen when prolonging accelerated ageing, the value recorded after 30 days being of 1.45.

Table 1
Concentration of carboxylic acids in paper

Accelerated ageing (days)	Formic acid (mg/g)			Acetic acid (mg/g)		
	Samples A (Control)	Samples B (MgO)	Samples C (MgO + MMMC)	Samples A (Control)	Samples B (MgO)	Samples C (MgO+ MMMC)
0	0.185±0.070	0.370±0.019	0.482±0.020	0.361±0.012	0.649±0.025	2.230±0.085
1	0.550±0.015	0.535±0.020	0.706±0.022	0.892±0.025	1.301±0.052	5.823±0.189
2	0.572±0.019	-	-	0.814±0.021	-	-
3	0.477±0.010	0.905±0.029	1.288±0.049	0.722±0.023	2.332±0.076	5.453±0.158
5	0.844±0.023	1.896±0.073	3.282±0.106	1.599±0.050	5.531±0.180	9.755±0.308
7	0.829±0.023	1.263±0.050	-	1.382±0.038	4.840±0.181	-
10	0.746±0.019	0.984±0.035	1.809±0.074	1.469±0.039	2.038±0.063	2.842±0.090
15	0.786±0.020	-	2.213±0.082	2.676±0.058	-	4.097±0.131
20	0.442±0.013	1.291±0.039	1.407±0.047	2.158±0.057	2.571±0.084	4.179±0.124
30	0.706±0.020	1.114±0.038	3.293±0.113	2.807±0.074	2.554±0.080	4.727±0.145
60	0.868±0.024	-	-	4.798±0.118	-	-

n = 3, RSD <4%
HPLC conditions: see EXPERIMENTAL

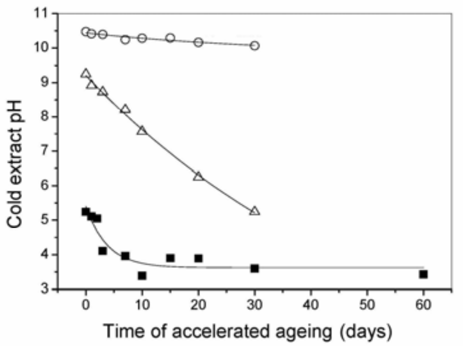

Figure 1: Influence of accelerated ageing at 98 °C and 50% RH on cold extract pH – (■) Sample A: control specimens, (Δ) Sample B: deacidified by dispersion of MgO, (○) Sample C: deacidified by mixture of MgO+MMMC (3:1)

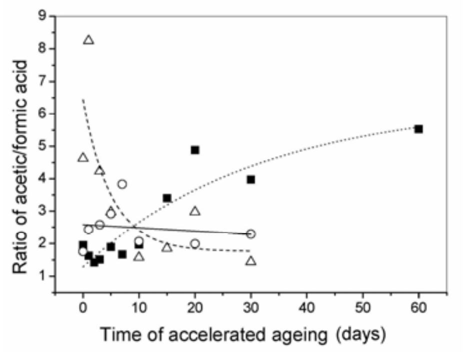

Figure 2: Influence of accelerated ageing at 98 °C and 50% RH on ratio of acetic/formic acids – (■) Sample A: control specimens, (Δ) Sample B: deacidified by dispersion of MgO, (○) Sample C: deacidified by mixture of MgO+MMMC (3:1)

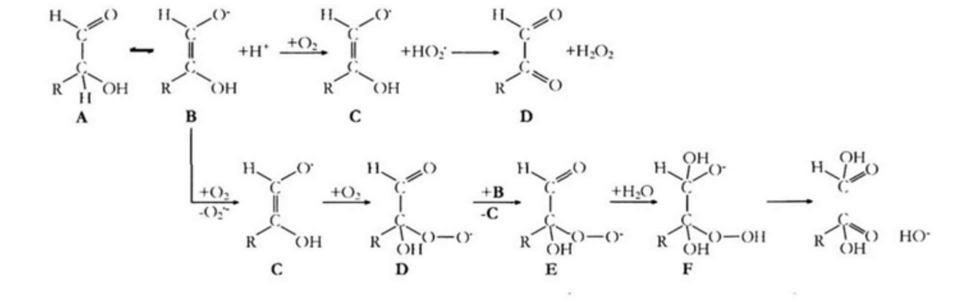

Figure 3: Two possible reaction pathways for oxidation of carbohydrate end-groups by oxygen in a mildly alkaline environment (R denotes the rest of a monosaccharide)[40]

The content of carboxylic acids in the modified specimens increased with prolonged ageing, as well as in the unmodified ones. On the basis of the measurement, it was noted that during accelerated ageing carried out on modified samples, a considerable increase in the concentration of acetic acid and formic acid occurred. These results suggest that the effect of modification with different contents of Mg^{2+} was an increased formation of carboxylic acids during accelerated ageing. The reason for this behaviour might be the strong promoting role of Mg^{2+} in increasing the concentration of acetic and formic acids *in situ*, during accelerated ageing at 98 °C and 50% RH.

The increased content of carboxylic acids during accelerated ageing may be due to an alkaline pH, since, in a cellulose macromolecule, probably only the aldehyde end-groups are capable of spontaneous reactions with oxygen, which are promoted by alkalinity. The mechanism of carbohydrate oxidation in an alkaline medium was reviewed[69] by Arts *et al*. (1997) and the reaction scheme presented in Figure 3 was proposed.[69,70]

As known, the rate of paper degradation and thus the amount of resulting degradation products depend on several factors, including the initial lignin content, type of fibres, content of metal ions, chiefly Al, Cu, Fe and others, the moisture content, acidity, as well as the manufacturing, storage and accelerated ageing conditions (temperature, relative humidity, stack or free hung sheets, exposure to light, etc.).[71] According to Zou *et al.*,[24] the loss of fibre strength is, in turn, due to cellulose depolymerisation, caused by acid-catalysed hydrolysis. These authors published in 1996 different results. It is unlikely that such an increase in acidity would have a significant effect on the rate of cellulose hydrolysis within the paper. Kinetic data published by Zou *et al.*[72] indicate that, for papers with a pH value above 4.5, the contribution of acid catalysis to the rate of cellulose depolymerisation by hydrolysis is only minor. But, according to recently performed studies,[49,50] acid hydrolysis causes chain scission of cellulose macromolecules and generates carbohydrates fragments. These fragments are oxidised to carboxylic acids, which generate an oxidation and hydrolysis cycle, thus enhancing paper acidity and causing autocatalytic paper degradation. This hypothesis would partially explain the concentrations of weak acids, such as formic, acetic, lactic, glycolic, oxalic, succinic, detected in naturally aged papers. The formation of these acids was also confirmed by other works.[34,36] Their mechanism of formation has not been determined in detail, but they are considered as products of the combined action of hydrolysis and oxidation.[34] The acidic products formed during accelerated ageing accumulate inside the paper and in the inter-sheet spaces of books or archival files, causing enhanced degradation.[73] In stabilisation 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, may cause paper stabilisation.[67] It is also evident that, during accelerated ageing, organic acids are formed, and may easily migrate in the loose-sheet materials. Accelerated ageing in stacks has been shown to increase the formation of organic acids. The presence of Mg^{2+} ions is evident from the increase in acetic and formic acids concentration, which is not relevant for unmodified samples.

In the presence of an acid (*i.e.* proton-donating ions H_3O^+, notation equivalent to H^+), the glycosidic bond is hydrolyzed and the macromolecules split into two shorter units.[73] Usually, the chemical reaction involves some elementary steps. In the first step, the addition of proton takes place, while later on it is removed from the reaction products acting as a catalyst.[73,4]

The degradation of polysaccharides occurs in two ways: random depolymerisation (a) and endwise peeling (b) (Fig. 4).

Since polysaccharides can be considered polycondensation products, their degradation, the reverse process, involves the hydrolysis of glycosidic bonds. The process occurs randomly along the chains and ideally results in the formation of monosaccharides.[74] Alkaline hydrolysis causes chain scission of the polymer chain and decreases the average chain length dramatically. Peeling removes one monomer unit at a time from the reducing end of the molecule.[75] This reaction does not influence the molar mass to any appreciable extent, unless very long processing times are used. Instead, the peeling reaction mainly influences the carbohydrate yields.[76] The properties of the cellulose chains determine the properties of cellulose fibres. The decrease in the polymerization degree of cellulose lowers the mechanical resistance of fibres, making them susceptible to shortening, as due to mechanical treatment.[77]

The addition of a Mg alkaline reserve has a manifold effect on the degradation mechanism – both curing and detrimental. On the one hand, it suppresses the self-acidification of paper produced during natural ageing, while, on the other hand, it accelerates the formation of acids. These are two competitive reactions. Also, paper alkalinization induces and endwise peeling reaction, providing substrates for acetic acid formation; however, it should have little effect on the overall depolymerization of the cellulose chains. The random alkaline degradation of polysaccharides is accompanied by the so-called peeling reaction of the terminal saccharide units. When subjected to strong bases, the cellulose chain ends can react and undergo the depolymerization reaction. This reaction explains the detrimental effect of excessively strong bases, such as calcium hydroxide particles, on paper permanence. When exposed to air, they are rapidly transformed into the corresponding carbonates, which do not induce this depolymerization reaction any more.[78]

To determine the course and result of alkaline degradation in polysaccharides, it is importnant to know the structural type of the saccharinic acid that is peeled off. If, for example, the terminal unit of the polysaccharide is lost as an isosaccharinic or saccharinic acid, the reducing terminal sugar unit of the polysaccharide will be re-established. If, however, a meta-saccharinic acid is formed at the end of the polysaccharide chain, degradation is stopped. If β-alcoxy elimination at C3 of the terminal unit of the polysaccharide proceeds, the reaction does not result in the loss of the terminal sugar unit; instead, this unit is stabilized in the form of meta-saccharinic acid.[75]

Jablonský *et al.*[79,80] found out that a substantial decrease (by 29.3%) in the degree of polymerization (DP) occurred even during a 24-h ageing, compared to the original control sample. A decrease by 71.6% (DP = 239) was observed after 720 h (30 days). The application of MgO dispersion as a deacidification agent slowed down process of degradation. After 720 h of artificial ageing, DP was equal to 415, which means a decrease of about 50.2%, compared to the sample deacidified by MgO during time t = 0 h. When 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.

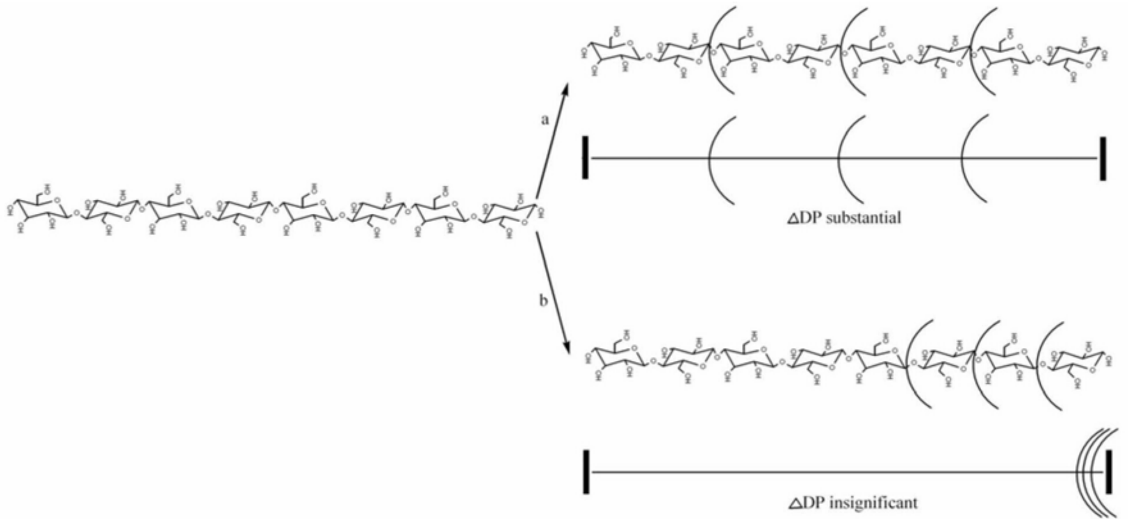

Figure 4: Two models of degradation of polysaccharides: a – statistically controlled, b – endwise peeling

Based on these results, we can say that the paper alkalisation increases the production of acetic and formic acids, as well as the content of magnesium salts of these acids in the modified paper. If Mg penetrates deeper into the structure of paper, then acid formation is more significant, as happened for samples C, compared to samples B.

On the other hand, despite an increase in acid production, a substantial reduction was observed in the degradation of modified samples. This suggests that the effect of Mg alkalisation is achieved by changing the extent of paper degradation. There is mainly peeling reaction and the mostly reaction secession of the end unit polysaccharide in the form isosaccharinic acid. In this way, smaller chain degradation of cellulose is achieved. Otherwise, the production of acids rises, rather than increasing the content of the acetate and formate in the paper.

Despite its inaccuracy, the use of folding endurance is widespread in paper permanence testing, because it is very sensitive to paper ageing.[81,82] It is very sensitive to ageing, compared to other mechanical or chemical properties.[83] The loss of folding strength (MIT double folds, load 0.3 kg) under accelerated ageing at 98 °C and 50% RH for unmodified paper (samples A) and for papers modified by MgO dispersion (samples B) and by MgO and methyl-methoxymagnesium carbonate (MMMC) mixture (3:1) dispersion (samples C) is shown in Figure 5.

Accelerated ageing lasting for more than 10 days causes folding strength (MD) to decrease considerably (the decrease in MIT double fold number amounts to 100%). After 7 days of accelerated ageing, the loss of strength was of about 89% (187 MIT double folds for 7 days) against unaged samples. After 10 days of accelerated ageing, the sheets presented 8 MIT double folds and the prolonged ageing decreased the number of MIT double folds to 1. The samples aged for more than 15 days showed small differences. In measuring the physical properties of weak papers, fold endurance is a definite disadvantage.[26] The decrease in folding endurance during accelerated ageing indicates that the groundwood newsprint paper becomes somewhat brittle.[84]

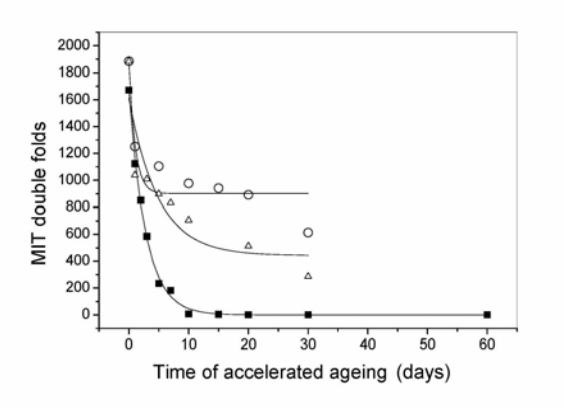

Figure 5: Decrease of folding endurance (MIT double folds) through accelerated ageing at 98 °C and 50% RH – (■) Samples A: control specimens, (Δ) samples B: deacidified by MgO dispersion, (○) samples C: deacidified by MgO+MMMC mixture (3:1)

Despite the fact that the modification of the paper samples by applying dispersion of MgO and of MgO and MMMC caused an increase in the content of carboxylic acids, it also achieved an increase in the mechanical properties of modified paper, compared to those of unmodified samples A. After the modification by MgO dispersion, the contents of acids amounted to 1.019 mg/g paper (0.37 mg formic acid/g paper and 0.649 mg acetic acid/g paper). The folding endurance was equal to 1885 for accelerated ageing of 0 days at 98 °C and 50% RH. The use of modified MgO had a positive effect on the increase of the folding endurance, compares to unmodified samples, where the MIT double fold = 1672. The positive influence of the modification by MgO and MMMC mixture was also verified (MIT double fold = 1884). Figure 5 shows that the loss of folding endurance during accelerated ageing at 98 °C and 50% RH depends on the influence of particular modifications. In the case of paper modified by the MgO and MMMC mixture, a smaller decrease of folding endurance during accelerated ageing was observed, compared to the samples modified by MgO dispersion. In both modifications, the lack of fibre brittleness expresses higher folding endurance, compared to unmodified samples. After 30 days of accelerated ageing, the increase of the loss of folding endurance at modification of dispersion of MgO 286 times against unmodified paper occurred. Samples C (modified by MgO and MMMC mixture), after 30 days of ageing, presented 2.14 times higher folding endurance than the samples modified by MgO dispersion. The analysis of sheet properties indicates that the loss of folding endurance is by far lower for the papers submitted to each of the two modifications, compared to unmodified paper, despite the fact that both modifications increased the content of acetic and formic acids.

CONCLUSIONS

The following can be concluded for accelerated ageing, at a temperature of 98 °C and 50% RH, of unmodified paper and paper modified by dispersion of MgO and MgO and MMMC mixture.

- The direct determination of the concentration of carboxylic acids *in situ* shows increased contents of acetic and formic acids during accelerated ageing.
- The increased content of the Mg^{2+} ions in the paper structure leads to increased contents of acetic and formic acids (respectively, acetate and formate) during accelerated ageing, in comparison with unmodified papers. The reason for this behaviour might be the strong promoting role of Mg^{2+} ions in the formation of organic acids.
- With the increase of the content of Mg^{2+} ions, the ratio of acetic/formic acids decreases in modified samples, compared to unmodified papers.
- The analysis of sheet properties indicates that the loss of folding endurance is by far less significant in papers submitted to both modifications, compared to unmodified paper, despite the fact that both modifications increased the contents of acetic and formic acids.

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