

L08 THE EFFECT OF MODIFICATION OF PAPER BY MAGNESIUM COMPOUNDS ON HORNIFICATION AND STRENGTH OF PAPER DURING ACCELERATED AGEING

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Introduction

Hornification is one of the main reasons leading to brittleness of fibres on paper recycling¹. Brittleness of recycled fibres is explained by hornification which is measured as a loss of the ability of fibres to retain water. This phenomenon was observed with lignin-cellulose fibres when they were repeatedly wetted and dried.

Hornification is one of the presumed processes occurring also during accelerated ageing of paper. However, the effect of hornification on changes in strength properties of paper has not been expressly proved so far. Hornification manifests itself in lignin-cellulose fibres as their lower ability to retain water and it is determined by WRV.

To determine the degree of hornification and to determine the changes on absorption of water, several methods can be used, for example the method determining the ability to retain water (WRV) or the method determining the point of saturation of fibres (FSP). WRV is calculated as a ratio of the mass of water in saturated fibres dipped into water, with subsequent removal of superfluous amounts of water in a centrifuge to the mass of absolutely dry fibres. The FSP is calculated as the total volume of pores, in other words the total content of water in the pores of the cell wall, and can be determined by free discharge or absorption of nitrogen. If the content of water is lower, WRV decreases linearly with increasing dry matter. This situation shows that hornification can occur when the content of water falls under critical level. If the content does not fall under FSP, hornification shall not occur. Both WRV and FSP fall in value when the fibres get repeatedly wetted, from dry state.

The chemical treatment, that is usually used to prevent hornification, gets effective under the condition that it disrupts the creation of hydrogen bonds between cellulose-cellulose and that it becomes strong enough to inhibit serious changes in the inner structure of the paper.

To prevent the process of hornification one can use chemicals that can cause the fibres to swell. Some studies have shown that alkalic NaOH causes the fibres to swell on the basis of ion-exchange reaction.²⁻⁶ The swelling occurs in reaction to osmotic pressure, generated by cations present in the solution (Donnan Effect). The level of swelling

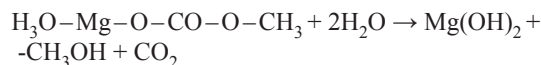
increases with the following order of cations: $Al^{3+} < H^+ < Mg^{2+} < Ca^{2+} < Li^+ < Na^+$.

The known modification processes that are to protect the lignin-cellulose carriers of information, as for example the Bookkeeper process⁷⁻¹¹ or the Wei T'o Canada^{9,12}, run on the basis of compounds that contain magnesium.

The neutralising agents for the Bookkeeper process are the particles of magnesium oxide (MgO) that are smaller than 1 µm and are dispersed in perfluorheptane. Some part of the content of magnesium oxide neutralises the present acids, while the non-regenerated part creates alkalic reserve. The magnesium oxide reacts with the acids and with the moisture in the paper in reactions described in the work¹³.

The deacidification agent of Wei T'o Canada is methoxy-magnesium-methyl-carbonate (MMMK). This alkoxide is soluble in organic solvents. It is an organic-metallic compound, having the formula: $CH_3O-Mg-O-CO-O-CH_3 \times xCO_2$, where x depends on solvents and on temperature¹⁴.

The MMMK reacts with the moisture of the paper, but most of all with the air humidity, as expressed by the reaction¹³:



There occur some other reactions liberating magnesium di-hydroxid $Mg(OH)_2$, magnesium carbonate $MgCO_3$ and magnesium oxide MgO , that react with the acids present in paper, thus creating neutral salts. The magnesium compounds, namely, $Mg(OH)_2$, $MgCO_3$ and MgO , gradually absorb the moisture and carbon dioxide CO_2 from the air to form basic magnesium carbonate $MgO \cdot MgCO_3 \cdot Mg(OH)_2$ that gets deposited into the fibres of the substrate, thus creating alkalic reserve that is able to protect the paper against acids.

The end-products from the previously mentioned reactions have a deacidification effect on the products of acid hydrolysis in the paper. Simultaneous swelling reactions of the fibres can occur and they lead to increased flexibility and antihornification effect.

This study reports on the effect of some magnesium compounds on improved ability of fibres to retain water in the process of accelerated ageing. The ability to retain water is a measure of hornification that is one of the mechanisms of fibre brittleness.

Experimental

Thermally Accelerated Ageing

Paper samples held 24 hours in climatic conditions at 23 °C, and RH = 50% were put in sacks made of layered polyethylene foils with aluminium layer and hermetically closed. The sacks were conditioned at temperature $t = 98 \pm 2$ °C, in time periods 0, 1, 2, 3, 5, 10, 15, 20 and 30 days according to standard ASTM D 6819-02 ref.¹⁵.

Paper

The experiment was performed on newspaper produced by Jihočeské papírny Větrní a.s. The newspaper was wood-

based, callendered, nonsized, with basis weight 45 gm^{-2} , containing 55 % bleached ground wood pulp, 20 % white sulphate pulp, 15 % trapped waste fibres, 10 % clay, pH (surface): 4.5–5.0.

Modification Suspensions

In the fight against the ageing processes, the procedures commonly used to modify paper are the processes Bookkeeper and Wei T'o. These processes are based on the concept of binding particles of magnesium compounds onto the paper fibre surface. Used modification suspensions were:

- Suspension of MgO in perfluorheptane (Bookkeeper), Preservation Technologies, L.P. (PTLP), Cranberry Township, PA (USA). The PTLP declares that their dispersion of Bookkeeper contains three basic groups of components¹⁶.
- Methoxy-magnesiummethyl-carbonate in methanol, 2% solution, (MMMK), produced by SNK, Martin.

Measuring of Mechanical Properties

The tensile test to determine breaking length was performed on a universal tensile strength tester INSTRON 1122, Instron Ltd., High Wycombe, Buckinghamshire, England, pursuant to the specification *STN ISO 1924-1 (500340): Paper and cardboard. Determination of tensile properties. Changes of folding endurance*¹⁷ (w) were studied on modified and aged samples.

Water Retention Value

The test is carried out by placing a pad of moist fibers in a centrifuge tube that has a fritted glass filter at its base. The centrifuge is accelerated at 900 g to remove water from the outside surfaces and lumens of the fiber (a higher force is used according to some European standards). The remaining water is believed to be associated with submicroscopic pores within the cell wall. The centrifuged fiber pad is weighed, dried at 105°C , and then reweighed. The WRV equals the ratio of the water mass to the dry mass according to standard ISO 23718:2007.

Results

The previous works report that a modification by Bookkeeper is more or less just a surface modification and a modification of the paper by MMMK can be considered as running inside the volume because it is present in the whole volume of the paper. A similar difference can be found as to the content of magnesium in the paper on modification¹⁸.

Fig. 1. shows changes in the WRV parameter of modified papers as related to the period of ageing. The lowest slump of WRV is in connection with the non-modified paper. With the papers modified by compounds of magnesium, the decrease of WRV with time of ageing is less dramatic. The process of modification in surface, that works with a lower content of magnesium than the process of modification in volume, led to an increase of WRV by 17 %, while the modi-

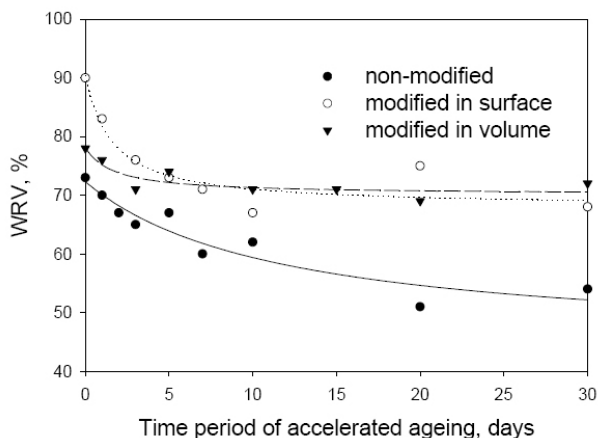


Fig. 1. WRV as a function of accelerated ageing time period for different modified papers

fication in volume saw the increase just by 5 %. When one compares the curve of this characteristic and how it develops during ageing, one can see that for the volume modification the trend of WRV to decrease is not significant, the value of WRV decrease is rather stable in the range between 78 % and 72 %. However, in the process of surface modification the WRV value falls from 90 % to 70 %.

When one compares changes of the relative WRV to the changes of WRV for non-aged paper, as dependent on time for given modification processes (Fig. 2.), the trends in decrease for this value are similar. With non-modified paper this relation has a decreasing characteristic, while with modified samples the decreasing trend looks as if it has stopped and is not continuing any more. Out of this relation the best seems to be the modification at which magnesium has been distributed into the whole volume of paper, as the decrease of relative WRV is the slightest. It could be caused by the moisture in the paper itself. Probably, during ageing of the paper, mag-

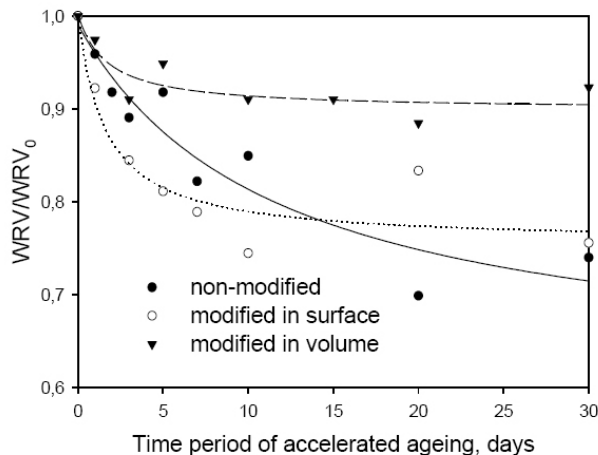


Fig. 2. Relative value of WRV that is a ratio of WRV and $\text{WRV}_{\text{time} = 0}$ as a function of accelerated ageing time period for different modified papers

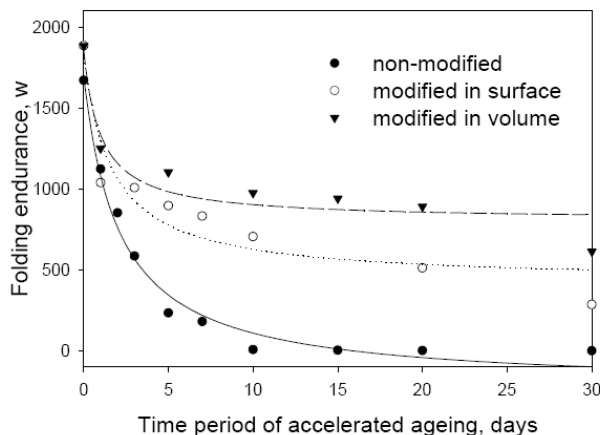


Fig. 3. Folding endurance as a function of accelerated ageing time period for different modified papers

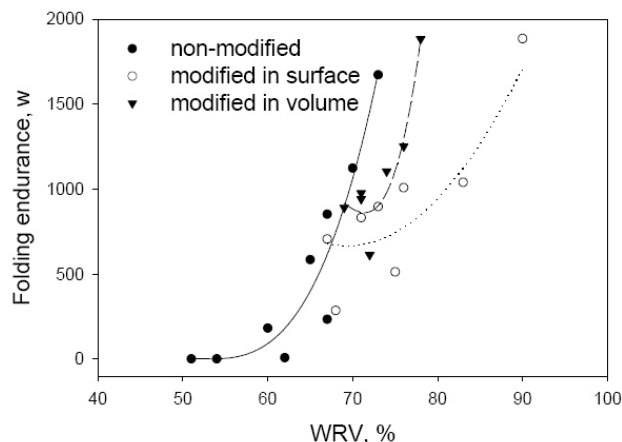


Fig. 5. Relationship between folding endurance and WRV

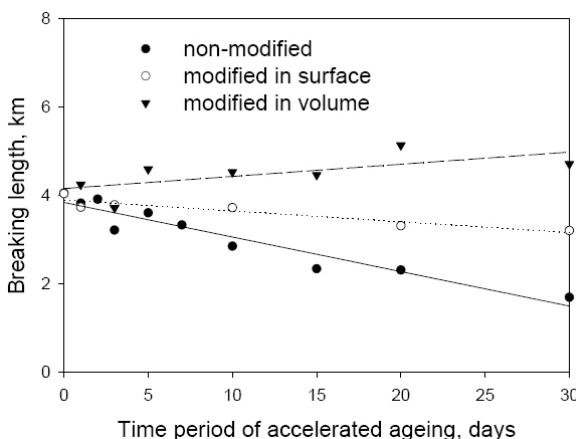


Fig. 4. Changes in breaking length during accelerated ageing for different modified papers

nesium reacted with the moisture present in the paper which caused swelling of the fibres, thus leading to better results of the process of hornification.

Fig. 3. shows the dependence of number of double-folds during accelerated ageing on time. The effect of magnesium compounds on the number of double-folds is clearly positive. Improvements in the number of double-folds can be seen also in non-aged samples, in which case the papers modified in volume or surface prove higher number of double-folds than non-modified paper. The curves reflecting the changes of double-folds are similar for all samples. The greatest decrease can be seen with the non-modified paper. All the samples show the greatest decrease in the number of double-folds in the first ten days of accelerated ageing, later there is a tendency to certain stabilisation of the decrease of the measured quantity. A similar development of relation can be seen for the WRV.

Fig. 4. shows dependences of breaking length on time of accelerated ageing. Even in this relation one can see the posi-

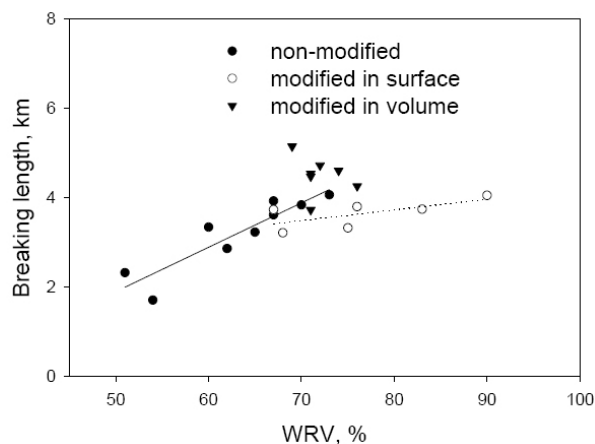


Fig. 6. Breaking length as a function of WRV for different modified papers

tive effect of paper modification via magnesium compounds. Even more, modification in volume increases the breaking length of paper during accelerated ageing. Similarly, paper modification in surface considerably contributes to its breaking length. In the case of non-aged papers, no differences can be seen for the parameter of breaking length.

Fig. 5. documents dependence of the number of double-folds on WRV of papers modified in different way. All the measured dependences reflect the fact that with growing values of WRV the number of double-folds grows as well. For non-modified paper the number of double-folds falls to zero. For modified papers the minimum values are considerably higher and they do not fall to zero.

For non-modified paper, the breaking length depending on WRV changes linearly, but with growing value of WRV the breaking length increases. For paper modified in surface, a similar dependence has been obtained, but with smaller angle of inclination. The paper modified in volume does not show this dependence.

Conclusions

Modification of lignin-cellulose fibres by magnesium compounds leads to their better retention of water. Modification by magnesium compounds inhibits hornification of fibres along the process of ageing. The probable mechanism of the modification is based on reaction of magnesium compounds that are transported into the paper in organic phase by water present in the paper. Magnesium compounds react with residual moisture giving alkalic substances that improve the ability of fibres to retain water. The fibres thus adjusted are more flexible; they undergo only a limited process of hornification and are more stable on bending than non-modified fibres.

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REFERENCES

- Gullichsen J., Paulapuro H.: *Papermaking Science and Technology, Book: 7: Recycled fiber and deinking* (Götsching L., Pakarinen H.), Fapet Oy, Helsinki, p. 359 (2000).
- Alanko K.: *M.Sc. thesis*, Helsinki University of Technology, Department of Forest Products Technology, Espoo, Finland, (1993).
- Scallan A., Tigerstrom A. C.: *CPPA 1st Research Forum on Recycling*, Montreal, p.149, 1991.
- Gurnagul N.: *Tappi J.* 78, 119 (1995).
- Katz S., Liebergott N., Scallan, A.M.: *Tappi J.* 64, 97 (1981).
- Laine J., Stenius P.: *Paperi Puu* 79, 257 (1997).
- Buchanan S. et al.: *An Evaluation of the BOOKKEEPER Mass Deacidification Process: Technical Evaluation Team Report for the Preservation Directorate*, Library of Congress. Preservation Directorate, Library of Congress. Washington 1994.
- <http://www.loc.gov/preserv/deacid/bkkeep2.html>
- Technical Evaluation Team Report: An Evaluation of the Bookkeeper Mass Deacidification Process*. Pittsburgh, PA, 1994.
- Supplement E.: An Evaluation of the Bookkeeper Mass Deacidification Process* (S. M. Melnick, Ed.), Preservation Directorate, Library of Congress, Washington (1994).
- <http://aic.stanford.edu/sg/bpg/annual/v15/bp15-17.html>
- Kaminska E. M., Burgess H. D.: *Evaluation of Commercial Mass Deacidification Processes: akzo-dez, Wei T'o. New and Artificially Aged Modern Papers*. Canadian Conservation Institute, Ottawa 1994.
- Kirschnerová S.: *M.Sc. Thesis*, Slovak University of Technology, Bratislava, Slovakia 2005.
- Brandt A. CH.: *Mass Deacidification of Paper. A Comparative study of existing processes*. Bibliothèque Nationale, Paris 1992.
- ASTM D 6819-02: *Standard test method for accelerated temperature aging of printing and writing paper by dry oven exposure apparatus*.
- Bieliková L.: *M.Sc. Thesis*, Slovak University of Technology, Bratislava, Slovakia 2005.
- ASTM D 2176 – 97a: *Standard Test Method for Folding Endurance of Paper by the M.I.T. Tester*
- Majerčáková K.: *M.Sc. Thesis*, Slovak University of Technology, Bratislava, Slovakia 2006.