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The efficacy of newsprint paper deacidification by carbonated magnesium propylate dissolved in heptafluoropropane

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Abstract

None of the existing methods conforms to the requirements of a genuinely "ideal" mass deacidification process. Beside the efficacy of deacidification processes, economic, safety and environmental risks are connected with the different systems.

The efficacy of stabilisation of highly lignified wood-containing paper by the carbonated magnesium propylate in the liquified gas of the 1,1,1,2,3,3,3-heptafluoropropane (HFC 227) was measured and compared with deacidification of the same paper by hexamethyldisiloxane, and air-water based deacidifying processes. The wood-containing paper test books were deacidified in Preservation Academy Leipzig, air-conditioned at the relative humidity RH = 50 %, and aged in sealed bags at 96±2°C.

The kinetics of folding endurance (ω), tensile strength (l_t) were measured and the indexes of relative increase of the lifetime ($S_{\tau,\omega}$), the folding endurance ($S_{\omega,t}$) and the tensile strength ($S_{lt,t}$) were calculated. The process was evaluated through multifactorial evaluation according to requirements of the Consortium Kniha^{SK} and the Library of Congress.

The deacidification by carbonated magnesium propylate dissolved in HFC 227 fulfilled neither the Consortium Kniha^{SK} nor the Library of Congress requirement for the lifetime increase ($S_{\tau,\omega}$=1.3). It did not improve the mechanical permanence of the wood-containing paper ($S_{\omega,15}$=1; $S_{lt,15}$=1.15). The comparative evaluation proved the superiority of the HMDO as well as air-water based deacidifying systems over the HFC based system for the wood-containing paper, which is an important sort of the paper in archives and libraries.

Keywords: efficacy, deacidification, carbonated magnesium propylate, heptafluoropropane, comparison

Introduction

To stop the degradation and save millions of books that are stored in archives, different technologies of deacidification and fibre strengthening have been invented (Proniewicz et al. 2001) and considerable efforts have been devoted to find new additives such as scavengers of free radicals, natural and synthetic compounds, inorganic compounds, solvents and to improve original technologies of deacidification (Cedzová et al. 2005; Cedzová et al. 2006, Cedzová and Katuščák 2006)

None of the existing methods conforms to the requirements of a genuinely "ideal" mass deacidification process, as it has been shown convincingly that each system has both its strengths and weaknesses (Porck 1996) Beside the efficacy of deacidification processes, economic, safety and environmental risks are connected with the different systems and limitations, more or less influencing the choice of the mass deacidification processes.

Application of mass deacidification process is connected with problems in controlling its efficacy and quality. There are no unified criteria for evaluating particular processes of mass deacidification (Banik et al. 2006). Alkaline reserve, pH, their homogenity and effect of deacidification agents are among those used within the scope of evaluation (Buchanan et al. 1994; Harris 1999; Swiss National Library 2004; Grossenbacher 2006) Nowadays, each organization brings own new parameters to evaluate the deacidification process. Evaluation according to the criteria of 'Library of Congress, Pittsburgh' (Buchanan et al. 1994) is one of the options. Another option is evaluation of the process efficacy according to criteria of Swiss National Library, Bern (Banik et al. 2006; Grossenbacher 2006; Banik 2005, Bluher 2003)

The carrier fluid of CSC Booksaver process is a liquefied gas 1, 1, 1, 2, 3, 3, 3-heptafluoropropane (HFC 227) and the deacidificant is carbonated magnesium propylate (n-propoxypropylmagnesiumcarbonate). The process is most closely related to the PAPERSAVE process, but differs from it in several important respects. The deacidificant of Booksaver (carbonated magnesium propylate) is distinctly less sensitive to the inadvertent exposure to water than the deacidificant employed by PAPERSAVE (magnesium-titanium-alcoholate or METE30 in hexametyldisiloxane). Because of the lower water-sensitivity of the Booksaver deacidificant, the materials to be treated do not have to undergo the intensive desiccation necessary for the PAPERSAVE treatment. Booksaver does not employ a flammable carrier fluid. The CSC Booksaver process was evaluated in report (Banik 2004).

Alkaline particles, such as MgO and dolomite micro-particles in the air-SoBu (www.sobu.de), MgO and CaO in the air-Libertec (www.libertec.de) and MgO in a perfluoralkanes-Bookkeeper (Buchanan et al. 1994) are also used in deacidification of books and archival documents containing cellulose base. The most significant effect of deacidification methods based on the application of sub-micron particles is a whitish powdery deposit on paper and binding surfaces, obviously the deacidification agent (magnesium oxide, calcium oxide, dolomite microparticles and calcium carbonate). It can be easily removed by brushing, but this creates additional and time-consuming work. If it remains in the book, it can spray out during the use with the risk of health problems for the user (Banik 2005).An important disadvantages of aqueous treatment is the solubility of certain pigments and adhesives used in books and other documents-Neschen (Porck 1996)

Experimental

Raw material

Wood-containing newsprint paper (grammage 45 g / m^2, surface pH: 5.6) containing mechanically bleached, groundwood (55%), bleached sulphite pulp (20%), scrap fibres (15%) and clay (10%) was used in the experiments. The test books (format A5) were sent for treatment to Preservation Academy Leipzig (PAL) company providing commercial mass deacidification.

Accelerated ageing procedure

Samples of paper were conditioned according to TAPPI T402 om -93 at 23±1°C, and at relative humidity of air RH = 50±2%. Seventy-five sheets of paper (A5 format) were encapsulated inside a PET / Al / PE bag. The samples were aged at 96±2°C for 0, 2, 5, 10 and 15 days according to ASTM D 6819 - 02: Standard test method for accelerated ageing of printing and writing paper by dry oven exposure apparatus, in which sealed glass tubes were replaced by a composite foil made of polyethylene / aluminium/ polypropylene (TENOFAN Al / 116S). After ageing, the papers were conditioned for testing according to TAPPI T402 - 93.

Mechanical properties

Breaking length was determined according to TAPPI T494 om - 88 and the folding endurance was determined using the MIT apparatus according to TAPPI T511 om - 96 with a tension of 0.3 kg instead of the standard 1 kg.

Evaluation of treatment effectiveness

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

$$S_{X,t} = \frac{X_{t,m}}{X_{t,n}} \qquad (1)$$

where $S_{X, t}$ stands for permanence coefficient by given treatment,
X - examined properties (the breaking length (l_t) and the folding endurance (ω)), t - ageing period.
If $S_{X, t} > 1$, the permanence is increased; if $S_{X, t} = 1$, it is not changed; $S_{X, t} < 1$, the permanence is decreased (Vrška et al.2004).

Linear dependence was obtained after calculating the logarithm of double folds. Time values for log ω = 0 were calculated from linear equation. Values were used for relative comparison the efficacy of deacidification process to non-treated control sample.

The lifetime of the paper ends when logarithm of the folding endurance becomes zero ($t_{\log \omega} = 0$)
The coefficient of relative increase of the lifetime for folding endurance ($S_{\tau, \omega}$) is to be expressed as:

$$S_{\tau,\omega} = \frac{t_{\log\omega=0,m}}{t_{\log\omega=0,n}} \qquad (2)$$

Results and Discussion

Kinetic dependences of changes in mechanical properties of paper were evaluated. Average values and average divergences that only indicate the variability recorded in measurements are given for all kinetic dependences.

Stability of the paper treated by carbonated magnesium propylate dissolved in heptafluoropropane (HFC 227) was compared to non-treated paper.
The loss of breaking length under ageing is shown in Figure 1.

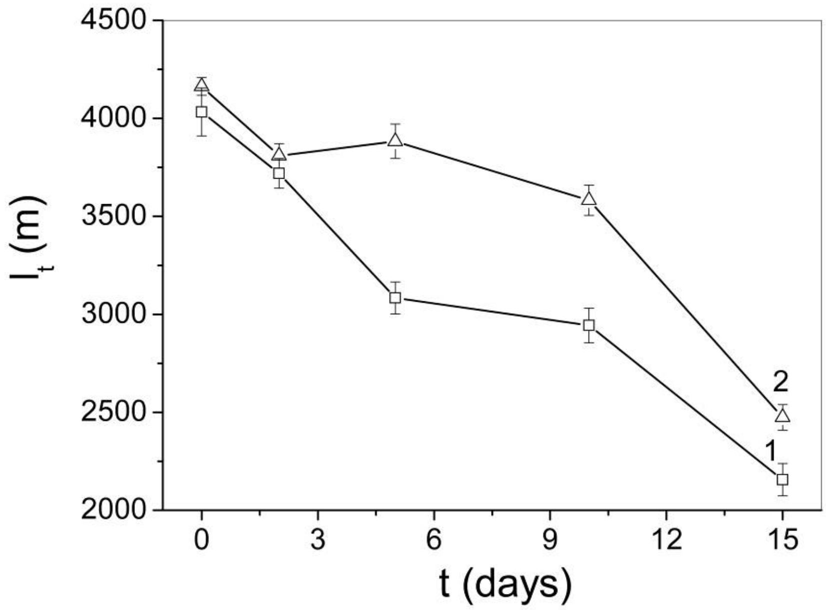

Fig.1. Effect of ageing time (t, days) on breaking length (l_t, m): 1 – non - treated newsprint paper, 2 - newsprint paper treated by carbonated magnesium propylate dissolved in heptafluoropropane

The breaking length of unaged non-treated paper was 4033 m. After 15 days of ageing, the loss of strength decreased by approx. 47 % (2156 m). After deacidification by carbonated magnesium propylate dissolved in HFC 227, the measured breaking length was 4163 m. After 15 days of ageing, the loss of strength decreased by approx. 41 % (2474 m). Permanence coefficient of the breaking length for unaged paper was evaluated $S_{lt,\,0}$ = 1.03, the modification did not caused strengthening effect. The permanence of breaking length after 15 days of ageing was $S_{lt,\,15}$ = 1.15, hence the modification caused positive stabilization effect. Despite its inaccuracy, the use of folding endurance is widespread in paper permanence testing, because it is very sensitive to paper ageing (Stadig and Hildering 1993; Hanus 2006). It changes more rapidly during the ageing process than other mechanical or chemical properties (Browning 1977). The loss of folding endurance (ω, double folds, load 0.3 kg) for non-treated and treated samples under accelerated ageing at 96±2°C is shown in Fig.2. respectively.

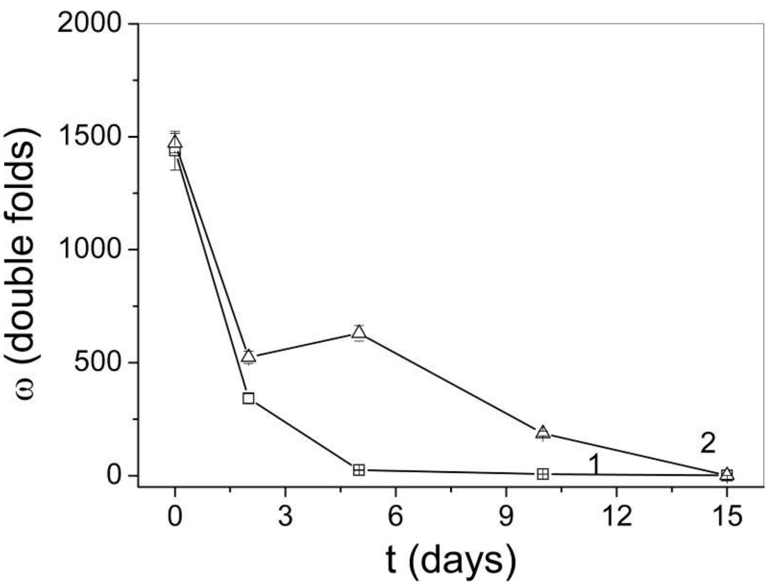

Fig.2. Effect of ageing time (t, days) on folding endurance (ω, double folds): 1 non-treated newsprint paper, 2 - newsprint paper treated by carbonated magnesium propylate dissolved in heptafluoropropane

The number of double folds of untreated paper was 1439. After 2 days of ageing, the number of double folds decreased rapidly (342). After 15 days of ageing, the folding endurance was reduced to 1 double fold. The permanence coefficient of folding endurance for unaged paper was evaluated $S_{\omega,0}$ = 1.02, which implies that the modification process did not result in strengthening effect.

After the modification by carbonated magnesium propylate dissolved in HFC 227, the determined double folds were 1472. After 2 days of ageing, the loss of strength was about 64% against to unaged modified samples. Stability increased significantly after 10 days of ageing reaching $S_{\omega,10}$ = 26.7, however, the deacidification by carbonated magnesium propylate dissolved in heptafluoropropane did not cause any stabilization effect ($S_{\omega,15}$ = 1) after 15 days of ageing.

The logarithm of folding endurance related to ageing time is shown in Fig.3.

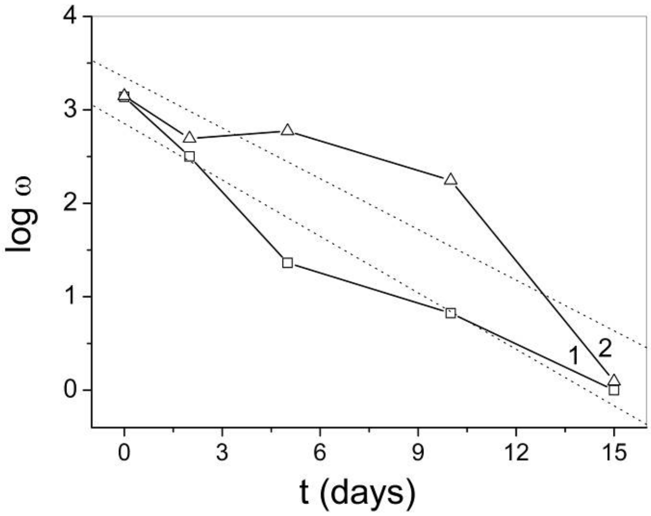

Fig.3. Effect of ageing time (t, days) on logarithm of folding endurance (ω, double folds): 1 - non-treated newsprint paper, 2 - newsprint paper treated by carbonated magnesium propylate dissolved in heptafluoropropane

Time values for log ω = 0 were calculated from linear equation. The coefficient of relative increase of the lifetime was calculated from formula (2).A part of the results presenting the mechanical folding endurance permanence evaluation is shown in Fig. 4. The order of deacidification processes quality was made based on the Consortium Kniha[SK], Bratislava, and Library of Congress (LoC), Washington methods. The requirement is as follows: the coefficient of lifetime prolongation $S_{\tau,\,\omega}$ must reach the value of 3 as a minimum.

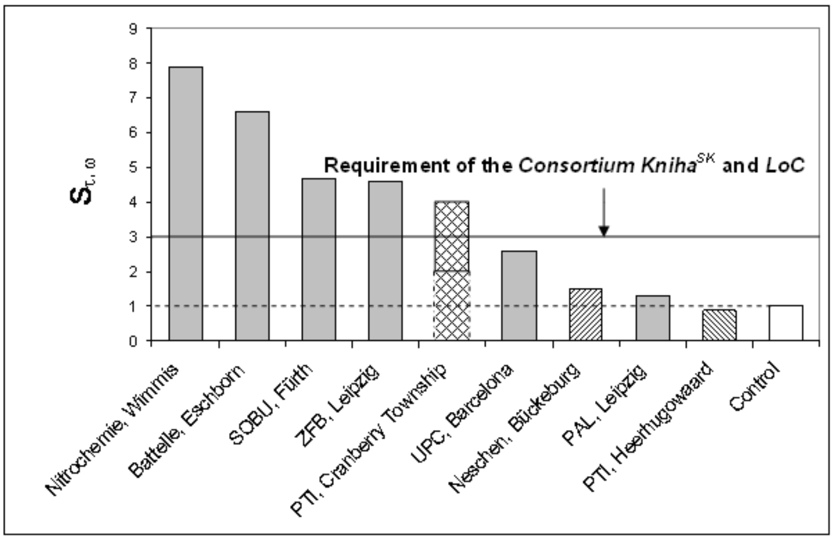

Fig.4. Comparative evaluation of deacidification efficacy based on the 2nd criterion of the Consortium Kniha[SK] Testing Lab, Bratislava and the Library of Congress, Washington ((Buchanan et al. 1994)

$S_{\tau,\omega}$ – coefficient of ageing time change; the index $S_{\tau,\omega}$ is related to a non-modified, non-deacidified control sample having $S_{\tau,\omega} = 1$.
Processes evaluated in the Consortium Kniha[SK] Testing Lab, the test books of A5 format (wood-containing paper, 55% of mechanical bleached groundwood, 20% of bleached kraft pulp, 15% scrap fibres and 10% clay, surface pH = 5.6), ageing conditions: accelerated ageing in closed bags from composite foil (PET-Al-PE), 96±2°C, 15 days (Majerčáková, Cedzová, unpublished).
Process evaluated in the Consortium Kniha[SK] Testing Lab, the test sheets of A5 format (wood-containing paper, 55% of mechanical bleached groundwood, 20% of bleached kraft pulp, 15% scrap fibres and 10% clay, surface pH = 5.6), ageing conditions: accelerated ageing at 105°C, 36 days (Grachová, unpublished)
Process evaluated in the Consortium Kniha[SK] Testing Lab, the test sheets of A5 format (wood-containing paper, 55% of mechanical bleached groundwood, 20% of bleached kraft pulp, 15% scrap fibres and 10% clay, surface pH = 5.6), ageing conditions: accelerated ageing in closed bags (PET-Al-PE), 96±2°C, 15 days (Majerčáková, unpublished)
Process evaluated at the IPST, Atlanta and at the LoC, various kinds of test sheets (pH = 5.7 – 9.42), accelerated ageing at 90°C and relative humidity 50% during 30 days.
Control – untreated paper of the same type as the treated / deacidified one.

Treatment of wood containing paper in the Preservation Academy Leipzig by carbonated magnesium propylate dissolved in heptafluoropropane has not met this requirement $S_{\tau,\omega} = 1.3$, which means that stability of modified paper increased by 130%. Stabilization effect on wood containing paper is relatively lower comparing to other deacidification processes.

To compare the carbonated magnesium propylate dissolved in heptafluoropropane technological platform (TP) to other recent TPs, the following criteria of multifactorial evaluation system of Consortium Kniha[SK] and Library of Congress (Buchanan et al. 1994) have been used:

1. Innovation potential. Potential of the future development, research, and further education.
2. Efficacy in term of increase stability of mechanical properties and life-time prolongation.
3. It is the criterion of efficacy of deacidification process according to the Library of Congress (Buchanan et al. 1994) on tested paper, which is expressed as the rate at which paper loses strength upon accelerated ageing at 90°C / 50 RH for up to 30 days, shall be decreased by at least a factor of 3.0, when the logarithm of the folding endurance is plotted against time in days ($S_{\tau,\omega}$). The permanence of the treated paper shall be increased by a factor of 300%.
4. pH and alkaline reserve,
5. Price
6. Risk
    - deterioration of documents, possibility of deacidification of books without their damage, sensorial properties

- explosion hazard
- flammability hazard
- health hazard
- environmental hazard

On the basis of criteria of multifactorial evaluation system the deacidification by the *n*-propoxypropylmagnesiumcarbonate (carbonated magnesium propylate) in the liquified gas of the 1, 1, 1, 2, 3, 3, 3-heptafluoropropane (HFC 227) did not fulfill the Consortium Kniha^{SK} and Library of Congress (Buchanan et al.1994) requirements for the lifetime increase ($S_{\tau,\omega} = 1.3$), did not improve the mechanical permanence of the wood containing paper ($S_{\omega,15}$=1; $S_{lt,15}$=1.15). The comparative evaluation proved the superiority of the HMDO as well as air-water based deacidifying systems over the HFC based system for the wood containing paper, which is an important sort of the paper in archives and libraries.

Conclusion

The efficacy of stabilisation of highly lignified wood containing paper by the n-propoxypropylmagnesiumcarbonate (carbonated magnesium propylate) in the liquified gas of the 1, 1, 1, 2, 3, 3, 3-heptafluoropropane (HFC 227) was measured and compared with deacidification of the same paper by hexamethyldisiloxane, and air-water based deacidifying processes. The folding endurance and tensile strength, as well as their stability in heat induced accelerated ageing at 96±2°C were measured. The multifactorial evaluation according to the requirements of Consortium Kniha^{SK} and Library of Congress was performed.

The deacidification by carbonated magnesium propylate dissolved in HFC 227 fulfilled neither the Consortium Kniha^{SK} and the Library of Congress requirement for the lifetime increase. It did not improve the mechanical permanence of the wood containing paper ($S_{\omega,15}$=1; $S_{lt,15}$=1.15). The comparative evaluation proved the superiority of the HMDO as well as air-water based deacidifying systems over the HFC based system for the wood-containing paper, which is an important sort of the paper in archives and libraries.

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References

Banik,G.(2004) Evaluation of the efficacy of CSC Booksaver Process for the deacidification for archives and library materials, based on test treatments at the preservation academy Leipzig (PAL), Fellbach, Austria;

Banik, G. (2005) Restaurator 26, 1:63 -75;

Banik, G., Doering, T., Hähner, U. (2006) International Conference SAVE PAPER, Bern,15 – 17.2. 2006, 94 – 109;

Bluher, A. (2003) Papier Restaurierung 4: 21 - 28;

Browning, B. L. (1977) Advances in Chemistry Series 164: 275-285;

Buchanan, S., Bennett, W., Domach, M. M. (1994) An evaluation of the Bookkeeper mass deacidification process, Pittsburgh, USA;

Cedzová, M., Gállová, I., Katuščák, S.(2006) Restaurator 27(1): 35–45;

Cedzová, M., Katuščák, S. (2006) Papír a Celulóza 61(1):10-12;

Cedzová, M., Vrška, M., Szeiffová, G. (2005), Chemické listy S(99): 442-444;

Grossenbacher, G. (2006) International Conference SAVE PAPER, Bern, 15 – 17.2. 2006,7 – 19;

Hanus, J. (1996) Alkaline paper advocate 9(1): 5-7;

Harris, K., E. (1999) A paper chase saving the written word at the Library of Congress, Washington DC, USA;

Porck, H. J.(1996) Mass deacidification. An update of possibilities and limitations, European Commission on Preservation and Access, Amsterdam, Netherland and Commission on Preservation and Access, Washington, USA;

Proniewicz, L. M., Paluszkiewicz, C., Wesenucha-Birczynska, A., Majcherczyk, H., Baranski, A., Konieczna, A. (2001) Journal of Molecular Structure 596: 163-169;

Stadig, C. J., Hildering, R. (1993) Restaurator 23(1): 18-25;

Swiss National Library (2004) Quality standards for the papersave Swiss process used for the deacidification of the collections of the Swiss federal archives and the Swiss federal office of culture, Bern, Switzerland;

TAPPI T402 om - 93 Standard conditioning and testing atmospheres for paper, board, pulp handsheets, and related products;

TAPPI T494 om - 88 Tensile breaking properties of paper and paperboard (using constant rate of elongation apparatus);

TAPPI T511 om - 96 Folding endurance of paper (MIT tester);

Vrška, M., Katuščák, S., Polovka, M., Vizárová, K., Cedzová, M., Hanus, J., Mináriková, J., Bukovský, V. (2004) Wood Research 49: 53 - 62;

www.libertec.de, 2008-08-08;

www.sobu.de, 2008-08-08