L03 EFFECT OF HEXAMETHYLDISILOXANE SOLUTION OF ZIRCONIUM PROPOXIDE ON PERMANENCE OF PAPER

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Introduction

Ageing of lignocellulosic carries of information is natural process influenced by different factors. Of the outdoor impacts, relative humidity, oxides of sulphur and nitrogene and others, while of the indoor factors, type of fibres, sizing agent, filling agent, etc. may be introduced[1,2,3].

Influence of ageing leads to formation of other compounds, which accelerate degradation of paper, e.g. organic compounds[4,5,6].

To stop ocurring these processes, conservation techniques, such as deacidification of paper are used[7]. Efficient deacidification systems have been applied in both polar and nonpolar medium in conservation practice. If this modification system is in the polar medium, it is supposed that diffusion of low molecular compounds to the cell wall, fibrils, microfibrils, elementary fibrils and to the molecular level of other units are to be performed.

Double alkoxides, combination of chemical elements Al-K, Sn-Mg, Zr-Ca are used as a neutralizing agent in suitable solvents, such as alcohols, fluoro-chlorohydrocarbons, hydrocarbons and siloxanes. Disadvantage of the above mantioned alkoxides lies in the formation of visible deposit[8,9].

For papermaking industry, water solutions of zirconium compounds are of particular importance, for example adhesions supporting cohesion to the different surface, etc[10].

This work was aimed at verifying the effect of hexamethyldisiloxane (HMDO) solution of zirconium propoxide on the permanence of newsprint paper.

Experimental

Raw Materials

Newsprint paper with extract pH 5.5–6.0; grammage $m_s = 45\ g m^{-2}$, containing 55 % of mechanical bleached groundwood, 20 % of bleached kraft pulp, 15 % scrap fibres and 10 % clay was used as received.

Modification System

Two different solution of zirconium propoxide (70 % wt. in 1-propanol, Aldrich) in hexamethyldisiloxane (≥98 %, Aldrich): 0.02M solution and 0.04M solution were used.

Sheets were modified for 10 minutes at regulat stirring in a laboratory shaker. Subsequently, sheets were dryed free in sieves.

Accelarated Ageing

Samples of paper were conditioned for 24 hours at T = (23 ± 1) °C, RH = (50 ± 2) % before the accelerated ageing. Subsequently were aged in hermetically sealed bags at 98 ± 2 °C during 0, 1, 2, 3 and 5 days according to standard ASTM D 6819-02[11].

Property Measurement

Changes of folding endurance[12] (ω), breaking length[13] (lt), Kubelke-Munke intensity of 1,735 cm^{-1} peak by FTIR[14] (KM intensity), $pH_{extract}$[15] and total color difference[16] (ΔE) were studied at modified and aged samples.

Folding endurance was expressed as a coefficient of permanence[17, 18] in the time of ageing (t):

$$S_{\omega,t} = \frac{\omega_{\text{modified},t}}{\omega_{\text{control},t}} \qquad (1)$$

- if $S_{\omega,t} > 1$ – permanence increased
- if $S_{\omega,t} < 1$ – permanence decreased
- if $S_{\omega,t} = 1$ – is it not change.

Results

The permanence of paper samples modified with HMDO solution of zirconium propoxide was studied. Permanence of paper was evaluated by the change of folding endurance (ω), breaking length (lt), KM intensity of 1,735 cm^{-1} peak (KM intensity), $pH_{extract}$, and total color difference (ΔE).

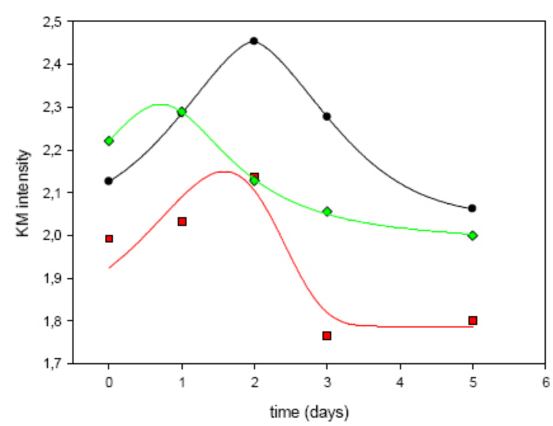

Fig. 1. **Depedence of KM intensity peak 1,735 cm^{-1} on the time of accelerated ageing obtained by evaluation of FTIR DRIFT spectra of control (•) and samples modified by 0.02M zirconium propoxide in HMDO (■) and 0.04M zirconium propoxide in HMDO (♦)**

Increased formation of carbonyls and carboxyls depends on time of ageing. In Fig. 1., values of KM intensity absorption peak at 1,735 cm^{-1}, which relate to binding vibration C=O groups are shown. Modification system restricts creation of carbonyls and carboxyls. Marked decrease of absorption peak at 1,735 cm^{-1} was observed at lower concentration of effective component compared with the control sample during the modification. This trend is held during all accelerated ageings. Higher concentration of zirconium propoxide in HMDO causes increased formation of carbonyls and carboxyls with unaged control sample immediately after the modidfication. However during the accelerated ageing a decrease compared with control sample is observed.

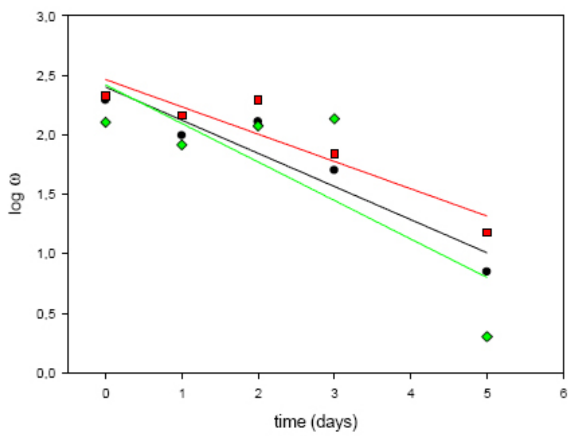

Fig. 2. **Dependence of common logarithm values of folding endurance during the accelerated ageing for samples modified by 0.02M zirconium propoxide in HMDO (■), 0.04M zirconium propoxide in HMDO (♦) and control sample (•)**

Folding endurance moderately increased at lower concentration of effective component ($S_{\omega,0} = 1.1$) just after the modification. During the accelerated ageing, stability values of folding endurance compared with unmodified control sample were followed. Stability effect of folding endurance after 5 days of accelerated ageing reached value 2.1 ($S_{\omega,5} = 2.1$). Higher concentration of zirconium propoxide in HMDO influences only slightly the folding endurance. It leads to an expressive decrease of this property after 0 and 5 days ($S_{\omega,0} = 0.7$ a $S_{\omega,5} = 0.3$).

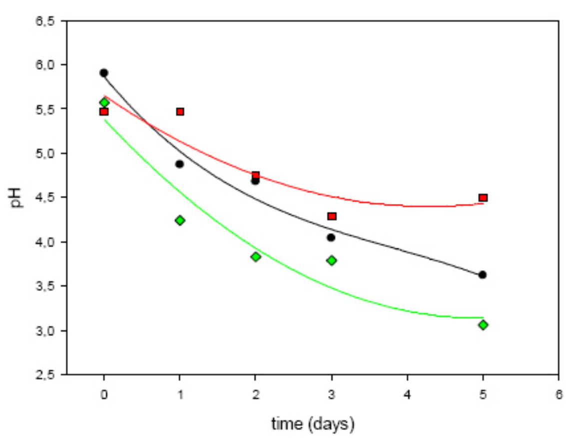

Fig. 3: Dependence of pH of cold extract samples modified by 0.02M zirconium propoxide in HMDO (■), 0.04M zirconium propoxide in HMDO (♦) and control – unmodified sample (•) during the accelerated ageing.

Cold extract of pH modified samples are comparable with unmodified sample (pH ≈ 5.5). However pH of sample with lower concentration of zirconium propoxide in HMDO (pH = 4.5) is more mild decreased after 5 days of accelerated ageing in comparison with unmodified control sample (pH = 3.6).

Table I
Breaking length values of samples modified with 0.02M zirconium propoxide in HMDO (0.02M), 0.04M zirconium propoxide in HMDO (0.04M) and unmodified samples (control) during accelerated ageing

Days	Control	0.02 M	0.04M
0	3,720 ± 570	3,860 ± 280	3,830 ± 410
1	3,760 ± 490	3,790 ± 390	4,000 ± 230
2	3,280 ± 670	3,770 ± 310	3,530 ± 550
3	3,600 ± 380	3,460 ± 490	3,560 ± 270
5	2,910 ± 430	3,340 ± 320	3,200 ± 380

Values of breaking length obtained from modified samples were higher than those of unmodified ones.

Samples modified with zirconium propoxide in hexamethyldisiloxane show decrease of measured properties in comparison with unmodified control sample. System of modification suppresses the formation of carbonyls and carboxyls. It indicates retardation of ageing process. Effect of modification causes that brittlenes of paper decreases and that folding endurance rises. Disadvantage of this modification system is low values of pH, which are comparable with unmodified paper. Combination of studied system with compound able to increase pH and thus alkaline reserve (for an instance MgO or other from lines of magnesium or calcium compounds) can help to solve this problem.

Advantage of this modification system is in the presence of polar element, 1-propanol, which is solvent of zirconium propoxide and at the same time, offers the use of non-polar carrier of effective compound. Non-polar solvent causes smooth surface of modified paper without warps and formation of visible deposits on the surface. Polar ingredient compiles presumption of facilitate intersection of effective zirconium compound to the structure of paper.

Lower concentration is more favourable in term of observed properties. This fact is shown on the look of modified paper. At a higher concentration of the effective component, e.g., at 0.04M solution, the total colour difference measured *vs.* the original unmodified paper is much more expressive (ΔE = 23.6) than that at at lower concentration of zirconium compound (ΔE = 17.5).

Conclusions

Solution of zirconium propoxide in HMDO exhibits a positive influence on the permanence of paper, and/or on measured properties. Utilization of studied modification system resulted in smooth surface of modified paper without warps and formation of visible deposits on the surface.

It leads to a decreased formation of carbonyl and carboxyl groups. There was also observed decrease intensity of the peak at 1,735 cm^{-1} (carbonyl groups) in comparison with control sample measured by FTIR.

It enhances the effect of stability of folding endurance – decreases brittleness of the measured sample in comparison with unmodified one.

Artificial ageing causes decrease of l_t by about 15 % in comparison with the control paper.

A more favourable effect offered solution of zirconium propoxide with lower concentration. Disadvantage of this system is its pH in comparison with pH of unmodified paper.

Combination of studied system with compound able to increase pH and thus alkaline reserve (for an instance MgO or other from lines of magnesium or calcium compounds) can help to solve this problem.

We thank to project of the Ministry of Education of Slovak Republic No 2003 SP200280301 Preservation, Stabilization and Conservation of Traditional Information Carriers of the Slovak Republic.

REFERENCES

1. Ďurovič M. et al: *Starnutie archiválií a knih*. Paseka, Praha 2002.
2. Porck H. J.: *Rate of paper degradation: the predictive value of artificial aging tests.* European Commission on preservation and access, Amsterdam 2000.
3. Barrow W. J.: *Deterioration of book stock: causes and remedies: two studies on the permanence of book paper*. Virginia State Library, Richmond 1959.
4. Shahani C. J., Harrison G.: *Works of art on paper, books, documents and photographs: techniques and conservation, Baltimore, United States, 2-6 September 2002*, p. 189.
5. Hroboňová K., Lehotay J., Jablonský M., Katuščák S.: *13th International Symposium on separation sciences and 13th AACI. Štrbské Pleso, High Tatras, Slovak Republic, June 27.-29., 2007.*
6. Figedyová S., Hroboňová K., Jablonský M., Katuščák S.: *5th International Student's Seminar. Chemistry and Technology of Wood, Pulp and Paper*, *Brno, Trade Fair EmbaxPrint, 21.5 2007*. poster presentation.
7. Porck H. J. *Mass Deacidification: an Update of Possibilities and Limitations on Preseravtion and Access.* Washington D. C., 1996.
8. Rauleder et al. (E. I. du Pont de Nemours and Copany): US Patent 6 294 682 (C08F 10/00).
9. Wittekind et al. (Battelle Ingenieurtechnik GmbH): US Patent 5 322 558 (B41M 7/00).
10. Lebtinen E.: *Pigment Coating and surface sizing of paper*. *Papermaking Science and Techmology, Book 11*. Fapet OY, Helsinki 2000.
11. ASTM D 6819-02: *Standard test method for accelerated temperature aging of printing and writing paper by dry oven exposure apparatus*.
12. ASTM D 2176 - 97a: *Standard Test Method for Folding Endurance of Paper by the M.I.T. Tester*
13. STN ISO 1924-2 50 0340: *Paper and board. Determination of tensile properties. Part 2: Constant rate of elongation method*
14. Polovka M., Polovková J., Vizárová K., Kirschnerová S., Bieliková L., Vrška M: Vib. Spectrosc *41*, 112 (2006).
15. STN ISO 6588 50 0381: *Paper, board and pulps – Determination of pH of aqueous extracts*.
16. Panák J. et al.: *Polygrafické minimum*. TypoSet, Bratislava 2000.
17. Katuščák S. et al.: *Preservation, Stabilization and Conservation of Traditional Information Carriers of the Slovak Republic.* State project of research and development, *Report* 2004.
18. Cedzová M.: *Disseretation*. Slovak University of Technology, Bratislava, Slovakia 2006.