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# Investigations of paper aging—a search for archive paper

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The change of mechanical (folding endurance index, breaking stress, breaking length, breaking index, tear index ), optical (brightness), chemical (cold extract pH, alkali reserve) and physical (water absorbency by surface, smoothness) characteristics of 5 paper samples were measured during the accelerated aging at 105 ± 2°C, and the measured exponential dependencies were described and fitted by the formal first-order kinetics. The statistic parameters of such fitting calculations evidenced good agreement of the experimental and calculated data. The relative decrease of each paper property corresponding to 48 days of accelerated aging was evaluated in order to compare the durability of paper samples. The best aging resistance was obtained for paper MAESTRO® Classic (SCP Ružomberok, Slovak Republic) and this paper material may be recommended for archival applications.


## 1. Introduction

The damage of paper materials upon aging is initiated by the irreversible breakage of their mechanical, chemical, optical and physical properties. This process is significantly influenced by the characteristics of paper obtained in the procedure of paper manufacturing (kind and quality of fibres, sizing materials, coatings, presence of acidic and metallic compounds), as well as by the external factors of paper materials storing (storage conditions, temperature, humidity, light, microbial and air pollutants, etc.) [1–5]. The loss of mechanical properties of paper documents fully eliminate the manipulation with the archival materials, and consequently their utilization as a source of information is impossible. Nowadays, an enormous effort in archives and laboratories is focused on the stabilization of acid papers by different deacidification procedures [6–10]. It was demonstrated that the efficient stabilization process required the removal of the reactive groups initiating the radical reactions in paper materials, and the additions of antioxidants [11]. The leading paper manufacturers are oriented on the production of acid-free graphic and office papers, however not all produced alkaline papers are suitable for the archival materials. Consequently a great attention is devoted to select suitable "stabile" paper for the printing of archival documents, and the permanence requirements of paper for documents were summarized in the standards STN ISO 9706 and ANSI/NISO Z39.48-1992. The investigations of accelerated aging of different paper samples under laboratory conditions bring useful information connected with the necessary paper durability, and enable the selection of the right paper for archival purposes [12–15].

Our study is oriented on the monitoring of mechanical (folding endurance index, i.e. double folds number/grammage, breaking stress, breaking length, breaking index, tear index, i.e. tearing resistance/grammage), optical (brightness), chemical (pH of cold aqueous extract, alkali reserve) and physical properties (water absorbency by surface, smoothness) of different paper samples during accelerated aging at 105 ± 2°C with the main aim to select the appropriate papers for archival materials in next centuries. We chose the standard aging method (STN ISO 5630) using hot air

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(105 ± 2°C) for the reason that it is very powerful and fast technique of accelerated paper aging. Three days under these storage conditions correspond to 25 years of natural paper aging [16]. Consequently, the results obtained during accelerated aging of paper materials can help to predict the changes in their characteristics for the period of hundredths of years.

## 2. Experimental procedure

### 2.1. Materials

The testing of paper properties during accelerated aging was performed with the following paper materials:

- A—standard offset paper (SCP Ružomberok, Slovak Republic);
- B—office paper ⊗ISO STN 9706 (SCP Ružomberok, Slovak Republic); this paper is declared as suitable for documents archivation.
- C—office paper MAESTRO® Classic (SCP Ružomberok, Slovak Republic);
- D—recycled office paper LPP 75 recy (Ludoprint Ltd., Trenčín, Slovak Republic);
- E—hand-made paper (Petrus, Bratislava, Slovak Republic).

Sodium hydroxide and hydrochloric acid were purchased from Lachema (Czech republic). The deionized water was used for the preparation of solutions.

### 2.2. Apparatus

The accelerated aging of paper substrates was studied in accord with standard ISO 5630-1 at 105 ± 2°C in the hot-air drying unit WSU 100 (VEB MLW Labortechnik, Illmenau, Germany) during the required time period (0, 8, 16, 24 and 32 days). The characteristic properties of the paper substrates before and after accelerated aging were measured according to the STN and STN ISO standards using the following instruments: automatically-operated micrometer, automatic analytical balance (Sartorius, precision of 0.001 g), apparatus for the folding endurance measurements (number of double folds at a standard tension of 9.81 N) according to Schopper (DFP, VEB Werkstoffprüfmaschinen, Germany), device for the water absorbency determination according to *Cobb*, universal apparatus INSTRON 1011 (England), apparatus for the smoothness evaluation (Büchel-Van der Korput, Netherlands) according to *Beek*, and filter photometer ELREPHOMAT DFC-5.

In accordance with the STN ISO 187 standard the paper samples were air-conditioned before measurements, which were carried out under the same conditions.

The pH values of the cold aqueous extracts were measured at 25°C by pH-meter OP-208/1 (Radelkis, Hungary) using a combined glass electrode.

## 3. Results and discussion

### 3.1. Characterization of paper substrates before accelerated aging

Tables I and II summarize the mean values of characteristic parameters, as well as the dominant mechanical properties measured for the original paper samples. Papers A, B and C are characterized with highest values

TABLE I The mean values of characteristic parameters determined for the original paper samples along with the standard specification used for the evaluation

| | Paper sample | | | | | |
|---|---|---|---|---|---|---|
| Parameter | A | B | C | D | E | Standard |
| Grammage (g $m^{-2}$) | 79.0 | 80.6 | 79.6 | 75.3 | 89.2 | STN ISO 536 |
| Thickness ($\mu$m) | 98.9 | 102.3 | 101.5 | 101.2 | 112.3 | STN ISO 534 |
| Specific weight (kg $m^{-3}$) | 799 | 788 | 784 | 744 | 794 | STN ISO 534 |
| Brightness (% ) | 95.6 | 91.9 | 95.4 | 69.7 | 81.7 | STN ISO 2470 |
| pH of cold extract | 9.4 | 9.0 | 9.3 | 8.7 | 6.6 | STN ISO 6588 |
| Alkali reserve (mol $kg^{-1}$) | 3.5 | 2.8 | 3.2 | 3.3 | – | STN ISO 10716 |
| Smoothness (s) | 48[a] 47[b] | 28[a] 27[b] | 39[a] 43[b] | 22[a] 22[b] | 17[a] 14[b] | STN ISO 5627 |
| Water absorbency by surface (g $m^{-2}$) | 48.6[a] 44.9[b] | 20.8[a] 21.0[b] | 38.8[a] 43.2[b] | 21.8[a] 25.1[b] | 14.9[a] 14.4[b] | STN ISO 535 |

[a]top side.
[b]underside.

TABLE II The mean values of fundamental mechanical properties measured for the original paper samples in machine (MD) and cross directions (CD)

| | Paper sample | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | A | | B | | C | | D | | E | |
| Parameter | MD[a] | CD[b] | MD | CD | MD | CD | MD | CD | MD | CD |
| Breaking stress (kN $m^{-1}$) | 3.9 | 3.2 | 4.7 | 4.5 | 3.7 | 2.9 | 1.8 | 1.6 | 5.1 | 4.9 |
| Breaking length (km) | 5.0 | 4.2 | 5.9 | 5.7 | 4.7 | 3.8 | 2.5 | 2.2 | 5.9 | 5.6 |
| Breaking index (Nm $g^{-1}$) | 49.3 | 40.7 | 58.2 | 56.2 | 46.6 | 37.0 | 24.4 | 21.3 | 57.6 | 55.2 |
| Tear index (mN $m^2g^{-1}$) | 7.61 | 6.30 | 7.34 | 6.33 | 7.69 | 6.48 | 5.58 | 5.19 | 1.66 | 0.34 |
| Folding endurance index ($m^2g^{-1}$) | 0.91 | 0.24 | 1.63 | 0.78 | 0.70 | 0.20 | 0.29 | 0.13 | 1.66 | 0.80 |

[a]machine direction.
[b]cross direction.

of brightness, sufficiently large alkali reserve, as well as with pH values of cold aqueous extract over 8.9. The origin of the recycled paper D is reflected in the brightness decrease and loss in the breaking stress, breaking length, breaking index, tear index and folding endurance index. However, this paper sustains high alkali reserve and pH of cold aqueous extract of 8.7. Paper samples A–D satisfied the requirements for the mechanical and chemical resistance of document papers specified in STN ISO 9706.

Paper E represents hand-made paper characterized with acceptable physical, mechanical and optical properties, however no alkali reserve was measured and additionally, the cold aqueous extract is acidic, therefore this paper is not able to neutralize acidic compounds produced during paper aging.

## 3.2. Characterization of paper substrates during accelerated aging

The properties of paper substrates were determined after 8, 16, 24 and 32 days of accelerated aging using hot air at $105 \pm 2°C$. According to the literature data we presupposed that 3 days of accelerated aging correspond to 25 years of natural aging [16].

The grammage, thickness and specific weight of all paper samples (A–E) were only negligible changed after 32 days of the accelerated aging, because we measured their relative decrease only below 1%.

The storage of paper documents and books in archives requires particularly the sufficient aging resistance of mechanical properties of paper samples, therefore we focus our attention on the determination of folding endurance index (double folds number/grammage), breaking stress, breaking length, breaking index and tear index (tearing resistance/grammage) during the accelerated aging.

Fig. 1a and b show the decrease of folding endurance index upon accelerated aging for papers A–D measured in machine (MD) and cross directions (CD). The decrease of folding endurance index and additionally, other paper properties as will be shown below, monitored during accelerated aging is exponential, and may be described by the formal first-order kinetics. Consequently, the experimental data were fitted by the exponential function (Equation 1) using least square analysis (program Scientist, MicroMath) and the corresponding values of $a$, $c$ and $k$ were calculated:

$$y = a \exp(-k t_{AA}) + c \qquad (1)$$

where $y$ is the monitored paper property, $t_{AA}$ is time of accelerated aging, $a$, $c$ are constants, and $k$ represents the formal first-order rate constant.

The statistic parameters of such fitting calculations (sum of square deviations, R-squared, correlation, coefficient of determination) evidenced good agreement of the experimental and calculated data. Using the evaluated constants ($a, c, k$) of each exponential decrease we estimated the values of paper properties after 48 days of accelerated aging, which represent 400 years of natural aging [16].

The relative decrease of each paper characteristic corresponding to 48 days of accelerated aging ($RD_{48}$) was calculated using Equation 2:

$$RD_{48} = \frac{y(t_0) - y(t_{48})}{y(t_0)} 100\% \qquad (2)$$

where $y(t_0)$ and $y(t_{48})$ is the paper property determined for $t_{AA} = 0$ day and $t_{AA} = 48$ days, respectively.

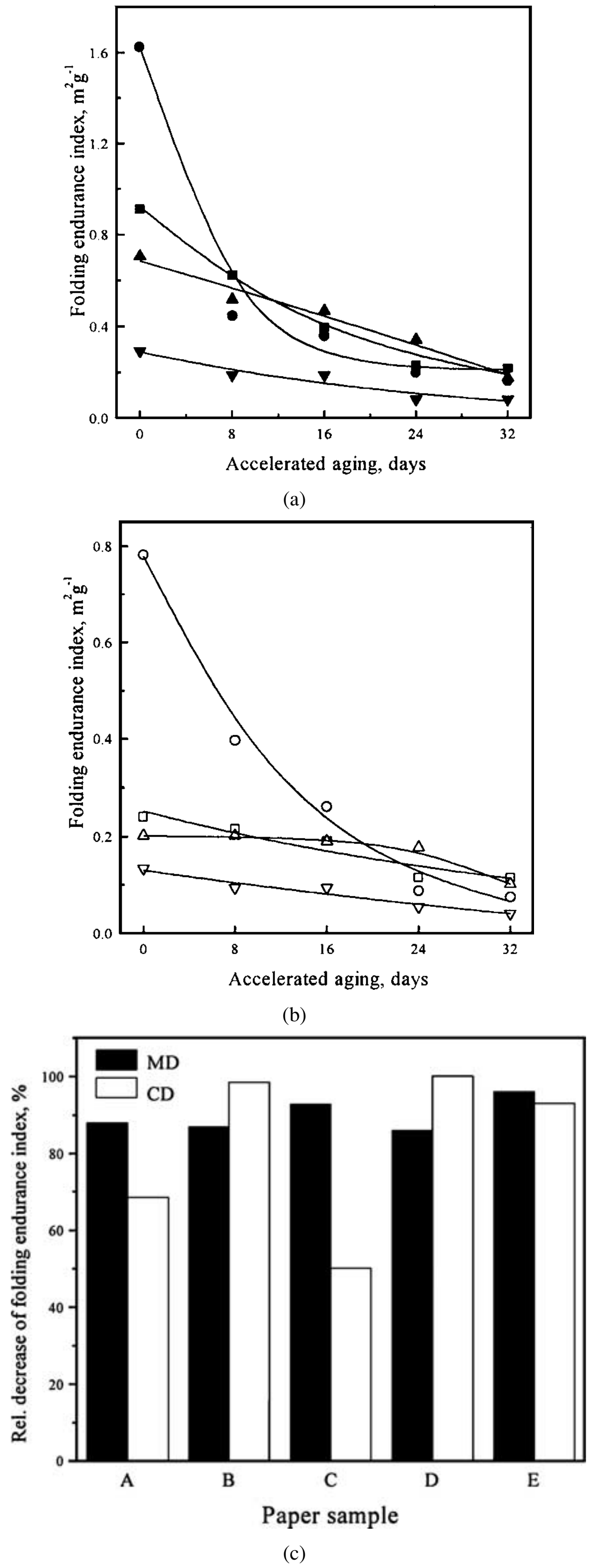



*Figure 1* The dependence of folding endurance index on the time of accelerated aging measured for paper samples A–D: (a) machine direction (■ A; ● B; ▲ C; ♦ D); (b) cross direction (□ A; ○ B; △C; ◇D). (c) The relative decrease of folding endurance index corresponding to 48 days of accelerated aging calculated according to Equation 2 for machine (MD) and cross directions (CD) of paper samples A–E.

TABLE III The calculated relative decrease of paper characteristics corresponding to 48 days of accelerated aging

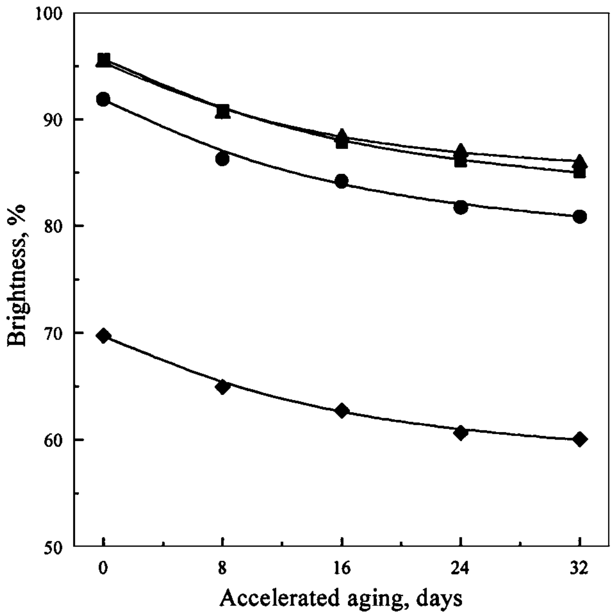
| | Relative decrease corresponding to 48 days of accelerated aging ($RD_{48}$) (%) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Paper sample | | | | | | | | | |
| | A | | B | | C | | D | | E | |
| Property | MD | CD | MD | CD | MD | CD | MD | CD | MD | CD |
| Breaking stress | 22 | 19 | 29 | 26 | 19 | 19 | 26 | 29 | 70 | 68 |
| Breaking length | 27 | 21 | 29 | 27 | 20 | 18 | 25 | 29 | 69 | 68 |
| Breaking index | 27 | 21 | 29 | 27 | 21 | 18 | 25 | 29 | 69 | 68 |
| Tear index | 33 | 32 | 36 | 40 | 20 | 20 | 24 | 24 | 77 | 63 |
| pH | 31 | | 21 | | 31 | | 7 | | 20 | |
| Alkali reserve | 11 | | 14 | | 19 | | 15 | | – | |

The relative decrease $RD_{48}$ evaluated for the investigated paper properties, was used for the comparison of the aging resistance of the examined paper samples (Table III).

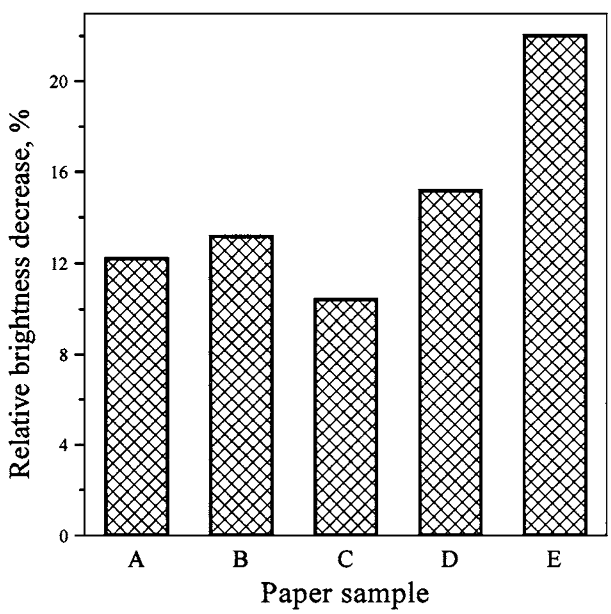
The schematic illustration of $RD_{48}$ of folding endurance index for the investigated papers is depicted in Fig. 1c. Our experiments confirmed that paper B, which fulfilled the standard STN ISO 9706 requirements, and which was originally characterized with very high value of folding endurance index (Table II), shows dramatic decrease already after 8 days of accelerated aging in both directions (Fig. 1a and b) and the value of $RD_{48}$ in cross direction grown up to 98%. Papers A and C possess better resistance to accelerated aging in folding endurance index, especially in the cross direction. However, for the recycled paper D we obtained very high loss in folding endurance index, as the values of $RD_{48}$ in cross direction reached 100%, and analogous significant decrease in both directions was observed for the hand-made paper E (Fig. 1c).

The influence of accelerated aging on breaking stress, breaking length, breaking index and tear index of paper samples was not so consequential as the monitored loss in folding endurance index (Table III). The best aging resistance in both directions was measured for paper C, as the relative decrease $RD_{48}$ was only about 20%. On the other hand, the hand-made paper E showed significant $RD_{48}$ changes over 60%, and consequently its application for the archival materials is not appropriate. Reactive compounds produced here upon accelerated aging, destroyed the cellulose fibers in this paper and significantly influenced its mechanical properties. Remarkably, the aging resistance of recycled paper D considering breaking stress, breaking length, and breaking index is comparable as was measured for office paper B, which was originally characterized by the highest values of these mechanical properties. Paper D additionally showed important durability in tear index (Table II).

The yellowing of paper materials and brightness decrease upon aging is the consequence of paper decomposition during the accelerated aging, as the application of dry/hot air caused the oxidation of cellulose backbone forming carbonyl chromophores. Fig. 2a illustrates the exponential decrease of brightness measured upon accelerated aging at 105 ± 2°C for paper samples




(a)




(b)

*Figure 2* (a) The dependence of brightness on the time of accelerated aging measured for paper samples A–D (■ A; ● B; ▲ C; ◆ D). (b) The relative decrease of brightness corresponding to 48 days of accelerated aging calculated according to Equation 2 for paper samples A–E.

A–D. The schematic comparison for the evaluated values of brightness $RD_{48}$ is depicted in Fig. 2b. The results obtained demonstrate the excellent brightness aging resistance for paper C, as the value of $RD_{48}$ evaluated for this paper was only 10%. The highest loss in brightness was observed for hand-made paper E ($RD_{48} = 22\%$) and for the recycled paper D ($RD_{48} = 15\%$).

The influence of accelerated aging on the chemical properties of paper samples was investigated monitoring the changes in pH of cold extract and in alkali reserve. The results measured for papers A–D are shown in Fig. 3a and b. The evaluated values of $RD_{48}$ shown significant drop of pH of cold extract and alkali reserve especially for paper C upon accelerated aging (Table III). Probably, this paper material was able to neutralize majority of the acidic compounds produced during aging, since its mechanical and optical properties showed the best aging resistance.

The distribution and size of pores and capillaries on the paper surface may be also substantially affected by aging [13]. The changes of water absorbency by surface and smoothness are of particular importance in the procedure of archival materials reconstruction, because the process of ink film formation on paper surface is quite different for the original and aged papers. The changes of water absorbency by surface and smoothness measured during accelerated aging at $105 \pm 2°C$ for top and underside of paper A are depicted in Fig. 4a and b. The water absorbency by surface considerably decreased after 8 days of accelerated aging, probably due to the morphological changes (e.g. increase of crystallinity) of the paper during dry/heat aging, but upon prolonged aging it was stabilized approximately on 50% of the original value (Fig. 4a). The smoothness of paper A exponentially decreased upon accelerated aging (Fig. 4b)

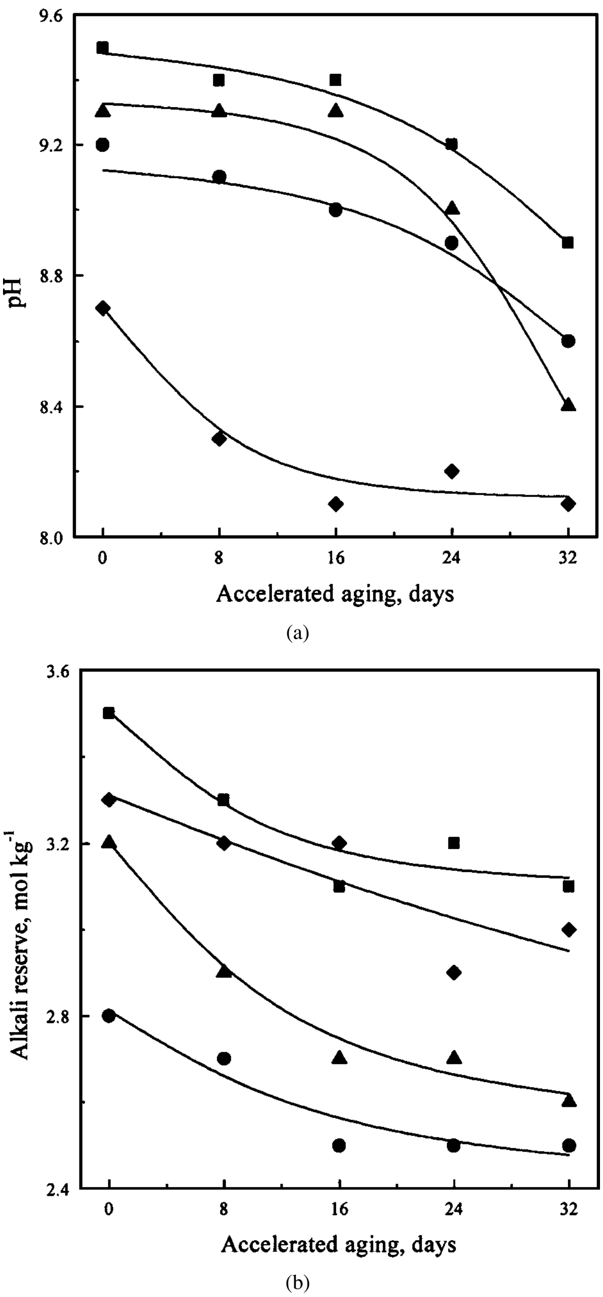



*Figure 3* The changes monitored during accelerated aging of paper samples A–D (■ A; ● B; ▲ C; ♦ D): (a) pH values of cold aqueous extracts; (b) alkali reserve.

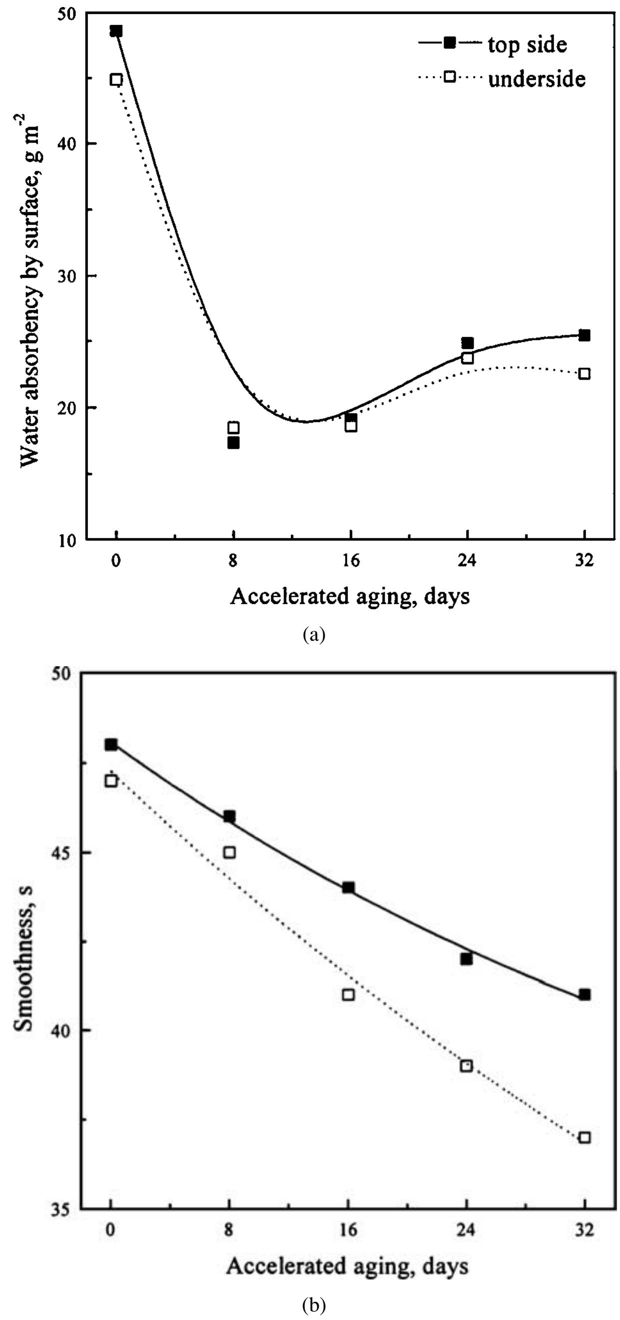



*Figure 4* The changes measured during accelerated aging of paper A (■ top side; □ underside): (a) water absorbency by surface; (b) smoothness.

in accordance with the damage of paper surface. In our study the lowest changes in water absorbency by surface and in smoothness were observed for paper C, in good correlation with the best aging resistance of this paper material monitored for mechanical and optical characteristics.

The presented comparison of four acid-free papers (A–D) and one acidic paper (E) demonstrated, that only paper C may be recommended for the applications in archives.

## 4. Conclusions

The mechanical, optical, chemical and physical properties of 5 paper samples produced in Slovak Republic were monitored during accelerated aging at $105 \pm 2°C$. The upon aging measured exponential decrease of the monitored paper characteristics was described by the formal first-order kinetics, and the experimental data were fitted using least square analysis. The values of relative decrease in paper characteristics corresponding to 48 days of accelerated aging were calculated and applied in the comparison of paper aging resistance. The best durability in a dry/hot environment was obtained for paper C (MAESTRO® Classic, SCP Ružomberok, Slovak Republic), and this paper material could be appropriate for printing of archival materials. On the other side the hand-made paper E (Petrus, Bratislava, Slovak Republic) represented acid-type paper and showed the consequential destruction of paper material upon aging, therefore its application for archives is not recommended.

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