

ACCELERATED AGEING OF WOOD-CONTAINING PAPERS: FORMATION OF WEAK ACIDS AND DETERIORATION OF TENSILE STRENGTH

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ABSTRACT

The deterioration process is generally the result of a series of reactions which lead to degradation of materials. Destruction of such materials is accelerated by the formation of weak acids from components used in paper production, mainly formic and acetic acids. These acids increase degradation of paper and at the same time they decrease mechanical properties. There is lack of detailed information on formation of acetic and formic acids in the process of accelerated ageing in connection with the loss of fibre strength in the available literature. This contribution presents information on the kinetics of acetic and formic acids formation during accelerated ageing determined by modified ASTM D 6819-02 (2002) procedure. The newsprint paper was aged from 0 to 60 days of accelerated ageing at temperature 98°C and 50 % RH in sealed 3 ply bags.

The ratio of acetic acid to formic acid concentration in situ increases during the accelerated ageing and is 2 times $\text{CH}_3\text{COOH}/\text{HCOOH}$ after 10 days and 5.5 times after 60 days. The loss of fibre strength due to degradation correlates well with the increase of the acetic acid concentration in situ and with the rising of $\text{CH}_3\text{COOH}/\text{HCOOH}$ ratio as well.

KEYWORDS: Paper ageing, acetic acid, formic acid, pH, tensile strength.

INTRODUCTION

The degradation of cellulose-based paper is important especially in archives and museums, where ageing in various conditions reduces the mechanical properties and deteriorates optical quality of stored papers, books and other artefacts (Kačík and Kačíková 2007, Kačík et al. 2007, 2008, 2009, Jablonský et al. 2011b). The degradation of the paper is considerably dependent on the raw material used for paper production, initial lignin content, sort of the fibres, content of metal ions chiefly Al, Cu, Fe and other, moisture content, acidity, it is also influenced by bleaching methods, mechanisation of the papermaking process (Barrow 1959, 1963, 1967, 1969, 1974, Bégin and Kaminska 2002, Hofenk de Graaff 1999) and the accelerated ageing (exposure to light, temperature, relative humidity, stack or free hung sheets, etc.) (Shahani et al. 1989, Pork 2000, Strlic et al. 2005a, b, c) and storage conditions (Bégin and Kaminska 2002).

The paper/material degradation process is complex multistimular process, where the main stimulæ are mechanical stress and damage, including for example prehistory of folding, abrasion, effect of mechanical impurities, exhibitions and other access etc., heat, light, oxidation, and biological stimulæ (Katuščák 2000, Katuščák et al. 2012).

The dominant degradation paths must be identified for a detailed understanding of the chemistry of cellulose degradation during/in ageing (Whitmore and Bogaard 1995). The process of degradation during ageing is accompanied to varying extents by degradation of the carbohydrate constituents, i.e., cellulose and hemicelluloses. One type of the reaction that is responsible for this degradation namely the acid hydrolysis reaction and may lead to considerable losses in degree of polymerization. These reactions generate a carbohydrate fragments which oxidize forming carboxylic acids. These acids enhance the acidity of the paper and thus initiate an auto-catalytic degradation cycle (Shahani 1994, Shahani and Harrison 2002). The process of hydrolysis and oxidations is very complicated. The mix of generated compounds depends on some factors. Factors influencing the degradation of lignocelluloses' materials to the monomeric sugar and the by-products (furfural, volatile, non-volatile acids and etc.) are: Properties of substrate, neutralizing capacity, proportion of easily hydrolysable holocellulose, amount and rate of hydrolysis of the difficult-to-hydrolyse materials, the length of the macromolecules, degree of polymerization of cellulose, configuration of the cellulose chain and another parameters is the acidity of system, concentration of acids and type in substrate, amount of acid released from the paper during hydrolysis and oxidations (Tahezadeh and Karimi 2007). The acid-catalysed hydrolysis of cellulose is generally described as a heterogeneous (pseudo-first-order) reaction in which catalytic systems in an aqueous environment react with the insoluble cellulose particles. It can be anticipated that the overall reaction rate of the hydrolytic degradation may be determined by mass-transfer effects related to the micrometer-scale dimensions and the crystallinity of cellulosic substrates (Van de Vyver et al. 2011).

Deterioration process is generally the result of a series of reactions (Unsworth and Mitchell 1990, Bayer et al. 1999, Margutti et al. 2001, Malesic et al. 2003, Strlic et al. 2003, Trnková and Bukovský 2003, Zou et al. 1994, Bukovský and Kuka 2001, Margutti et al. 2001, Dolenc et al. 2002) which lead to chain scissions which directly affect the mechanical properties (Barrow and Sproull 1959, Browning 1977, Černič-Letnar and Vančina-Kropar 2002, Gurnagul et al. 1993, Middleton et al. 1996, Stadig and Hildering 1993).

The compounds that are produced from the degradation of the lignocellulosic matrix are mainly carbonyl compounds such as aldehydes, ketones and carboxylic acids. During degradation of the lignocellulosic part, mainly formic acids, acetic acid and formaldehyde and a variety of acids and aldehydes are produced. A few studies have been committed to the analysis of the sub-products

from the age degradation of paper, using gas chromatography (GC), liquid chromatography (LC) and solid-phase microextraction (SPME) coupled with GC-MS (Belardi and Pawliszyn 1989, Bigourdan et al. 1996, Boyd-Boland et al. 2011, Clark et al. 2011, Doering et al. 2000, Doering 2007, Dupont et al. 2007, Gaspar et al. 2010, Hrivňák et al. 2009a, b, Hroboňová et al. 2009, Jablonský et al. 2008, 2011a, Lattuati-Derieux et al. 2004, 2006, Łojewski et al. 2010a, b, Shahani et al. 1989, Shahani 1995, Shahani and Harrison 2002, Strlic et al. 2007, 2009, 2011, Zhang et al. 1994). The formation of these acids leads to a self-promoting hydrolytic degradation chain reaction, or auto-catalysis (Baranski et al. 2004).

The accumulation of degradation products, such as acids, in the pores of fibres and inter-fibre spaces creates an autocatalytic effect, resulting in enhanced degradation (Baranski 2002, Barrow 1959, Bégin and Kaminska 2002, Dupont and Tétreault 2000, Menart et al. 2011).

Acidity is both the consequence of accumulation of acids in paper during degradation processes and the result of acids introduced into paper during production, and it is known that acidic papers are less stable compared to neutral or alkaline ones (Barrow 1959, Bégin et al. 1998). Alkaline papers showed appreciably higher rates of accumulation than did the other papers, since the acids formed are immediately neutralized and cannot enter into other reactions. These weak acids attach themselves strongly enough to paper, probably by hydrogen bonding, that they are not easily dislodged from the paper matrix (Porck and Teygeler 2000). Other workers have pointed the important role that acidic degradation products play in the ageing of the paper. (Frojd 1992, Shahani et al. 1989, Shahani 1994, 1995, Shahani and Harrison 2002) which showed us that acidic degradation products tend to accumulate inside polyester encapsulations and other enclosures, and thereby hasten the ageing of the paper (Shahani et al. 1989, Shahani 1994).

The present work has been carried out to investigate the generated acetic acid and formic acid and ratio of content acetic/formic acids in paper. The influence of the acids content on the tensile strength, folding endurance, surface and cold extract pH has been discussed.

MATERIAL AND METHODS

Raw material

Commercial wood-containing newsprint paper (grammage 45 g.m⁻²), pH determined by the 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 of the experiments.

Accelerated ageing at 98°C

Samples of paper were conditioned according to TAPPI T402 om -93 at 23 ± 1°C, and at relative humidity of air RH = 50 ± 2 %. The samples were subsequently aged according to ISO 5630 (2005), using modified temperature 98°C ± 2°C (instead of 100°C), and 50 % RH, corresponding to a paper humidity of 4–5 %. Twenty sheets of paper (A4 format) were encapsulated inside a PET/Al/ PE composite foil (Tenofan Al/116S) by sealing off all four edges using Polystar 30D impulse tong sealer (Rische & Herfurth, Hamburg, Germany). This bag was put into another PET/Al/PE bag and completely sealed off. Batches of samples were put into the thermostat for 0, 1, 2, 3, 5, 7, 10, 15, 20, 30 and 60 days and kept at the temperature 98 ± 2°C according to ASTM D 6819 (2002): Standard test method for accelerated aging 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). Humidity

inside the bag during accelerated ageing was $50 \pm 2\%$ and free air volume in the bag was 5 ± 1 ml. 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 acid, formic acid) were purchased in highly pure grades from Merck. 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 $25^\circ\text{C} > 5 \text{ M}\Omega\cdot\text{cm}$, $\text{TOC} < 30 \mu\text{g}\cdot\text{l}^{-1}$) were added. The mixture was kept to mix during 2 hours and subsequently filtered through a $0.45 \mu\text{m}$ filter. Amount of $20 \mu\text{l}$ filtrate was injected to the analytical column.

Instruments and conditions

The used HPLC system consists of a DeltaChrom SDS 030 isocratic pump, a 7125 Rheodyne injector with a $20 \mu\text{L}$ injection loop, a thermostat Model LCT 5100, a Knauer variable wavelength detector (set at 210 nm), and CSW32 software for peak identification and integration.

Chromatographic separations of acids were performed with column Polymer IEX H-form ($250 \times 8 \text{ mm I.D.}$, $8 \mu\text{m}$). The mobile phase consisted of $9 \text{ mmol}\cdot\text{L}^{-1}$ sulphuric acid. The column temperature was 20°C and the flow rate of the mobile phase was $0.8 \text{ mL}\cdot\text{min}^{-1}$.

Identification and Quantification

Formic and acetic acids were detected with spectrophotometric detection at 210 nm. The retention time was $9.7 \pm 0.2 \text{ min.}$ for formic acid and $10.7 \pm 0.1 \text{ min.}$ for acetic acid. The identification of the acids in water extract of paper was based on comparison of their retention factors (formic acid $k = 1.21 \pm 0.03$, acetic acid $k = 1.44 \pm 0.03$).

Calibration curves were constructed by performing a regression linear analysis of the peak area versus the acids concentration. Based on a four-point calibration, a linear response ($r = 0.99$) was observed from the limit of determination to $20 \text{ mg}\cdot\text{mL}^{-1}$ of studied acids.

The limits of detection, defined as the lowest sample concentration, which can be detected (signal-to-noise ratio of 3:1) were $10.7 \mu\text{g}\cdot\text{mL}^{-1}$ for formic acid and $18.4 \mu\text{g}\cdot\text{mL}^{-1}$ for acetic acid. The limits of determination, defined as the lowest sample concentration, which can be quantitatively determined with suitable precision and accuracy (signal-to-noise ratio of 10:1) were $42.8 \mu\text{g}\cdot\text{mL}^{-1}$ for formic acid and $92.2 \mu\text{g}\cdot\text{mL}^{-1}$ for acetic acid.

On the Fig. 1 chromatograms of separation of formic acid (1) and acetic acid (2) are shown in water extracts of paper (sample A) after 0, 7, and 60 days of accelerated ageing at temperature 98°C and RH 50 %.

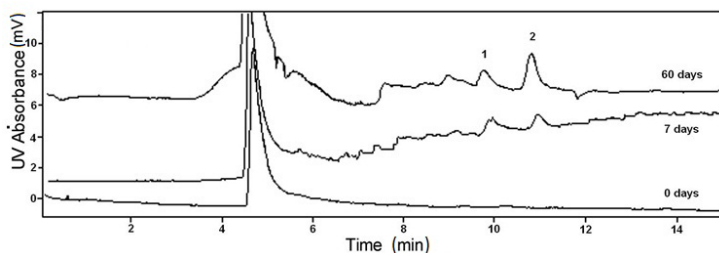


Fig. 1: Chromatograms of separation of formic acid (1) and acetic acid (2) in water extracts of paper after 0, 7, and 60 days of accelerated ageing at temperature 98°C and 50 % RH. HPLC conditions: see experimental part.

Surface and cold extract pH

Surface pH was measured according to TAPPI T 529 om-88 (pH of paper surface using a flat combined glass electrode) and cold extract pH was measured according TAPPI T 509 om-02 (cold extraction, 1 g of sample per 70 mL of water, 1 h).

The precision in pH determinations of cold extract and surface pH are estimated to be ± 0.2 units, respectively.

Each data point represents the average value of five independent measurements for surface pH and three measurements for cold extract pH.

Mechanical properties

Tensile strength was determined according to TAPPI test Method T494 om – 88.

RESULTS AND DISCUSSION

The deteriorative effect of acidity in paper has been known for many years. The pH value is the frequently checked parameter in paper conservation research. Acidity measurements also give an indication of the mode in which the material influences its degradative behaviour. Several pH methods have been applied to describe quantitatively the effects of ageing on paper support and acidity in historical paper (Joel et al. 1972, Ray 1972, Strlic et al. 2004, 2005a, 2007, Flynn and Smith 1961). To determine the pH affects there are many factors such as salts, sizing materials, fillers, and coating, raw materials, other additives and various chemical and physical reactions. Their action is not quite evident. These reactions occur simultaneously during the time of flat electrode pH measurement, the conditions for establishment of equilibrium in these processes are not satisfied (Ray 1972). The measurements of a flat electrode are often used mainly due to the speed setting and quasi non-destructive method for setting. It is desirable to select a definite procedure and follow it closely, so that the readings was consistent and had maximum diagnostic value. The method used should be described accurately so as to aid others in the interpretation of results.

Change of pH (cold extract pH and surface pH) during the accelerated ageing of papers at 98°C, 50 % RH was noticed. The correlation between surface pH, cold extract pH and the time of accelerated ageing of paper (Fig. 2) was established. Results in Fig. 2 show that the observed surface pH and cold extract pH decrease with the longer time of ageing. At the accelerated ageing at the temperature 98°C, 50 % RH was achieved smaller decrease of surface pH than of the cold extract pH.

A correlation between pH values determined as cold extract pH versus surface pH is presented on Fig. 3. Correlation coefficient between both above mentioned pH was 0.81. Relationship between concentration of acetic acid and formic acid and surface pH expressed for paper ageing is shown on Fig. 4.

Strlic et al. (2007) determined that in the observed pH range (5.5 – 9) the emission of acetic acid was independent on sample pH. This fact was explained by existing acetic acid mainly form of acetate (pH above 5). In this paper small correlation ($R^2 = 0.53$) between concentration of formic acid generate during the accelerated ageing and surface pH was found. The correlation between the acetic acid content and surface pH has also been observed and correlation coefficient in this case was 0.92. The results clearly showed that the concentration of formic acid was not markedly varied with pH in the observed pH range, while that of concentration of acetic acid was. A satisfactory correlation between acetic acid and pH was determined.

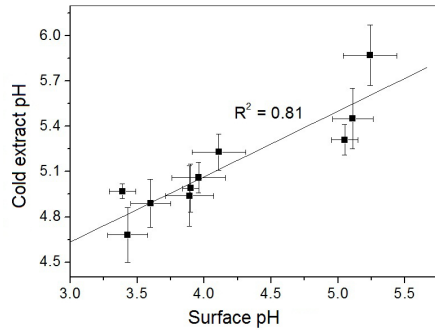
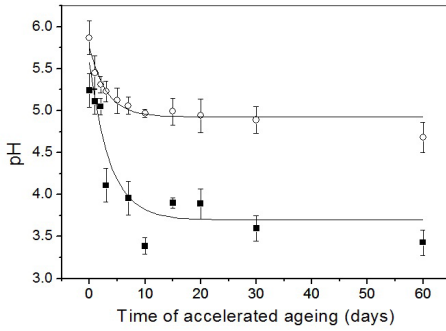


Fig. 2: Influence of accelerated ageing at the temperature 98°C, 50 % RH on the surface and cold extract pH.

Fig. 3: Cold extract pH vs. surface pH. The accelerated ageing at temperature 98°C and 50 % RH.

■ – surface pH
○ – cold extract pH

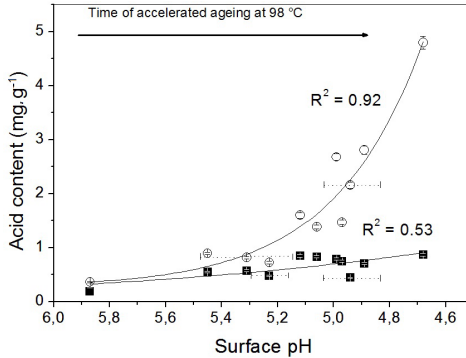


Fig. 4: Influence of acid content on the surface pH. The accelerated ageing at temperature 98°C and 50 % RH.

The mechanism of acidic hydrolysis is rather known (Baranski et al. 2005, Mosini et al. 1990, Zou et al. 1996). Oxidation mechanism during natural and accelerated ageing is much less abundant (Ali et al. 2001, Calvini and Gorassini 2002, Calvini et al. 2007, 2008, Emsley et al. 2000, Łojewska et al. 2005a, 2006, 2007, Łojewski et al. 2010a, b, Margutti et al. 2001, Strlic et al. 2005b, c). The oxidation propagates through consecutive and parallel paths (Łojewska et al. 2005b, 2006) lead to the formation of various carbonyl groups. Hydrolysis and oxidation are tangled together (Łojewska et al. 2005a). The formation of carboxylic groups upon oxidation promotes hydrolysis and vice-versa; hydrolysis generates new reducing end groups for oxidation. The self-generated acidic compounds from cellulose accelerate the degradation of the substrate. Crystalline regions of the cellulose are less accessible to reactive species; on the other hand, amorphous regions are easily penetrated due to the local chain disorder which gives to this fraction a faster rate of depolymerization (Gehlen 2009, 2010, Calvini et al. 2007, 2008). However, if the produced acidic compounds are volatile species, then their release under low pressure will reduce the global rate of degradation of cellulose (Gehlen 2010). The degradation of

cellulose by acid catalysis is a heterogeneous process that has several steps of the macromolecular chain scission to form low molecular weight products (Stephens et al. 2008, Xiang et al. 2003a, b). Levulinic, propionic, acetic and formic acids are usually found during cellulose degradation (Shahani and Harrison 2002).

The relationship between ratio of acetic acid/formic acid and time of accelerated ageing at 98°C and RH 50 % is shown in Fig. 5 and the correlation coefficient is 0.86. It was found that the molar ratio of acetic acid to formic acid is 2, when the accelerated ageing was carried out up to 10 days at the temperature of 98°C, 50 % RH. At a longer time period of accelerated ageing the formation of acetic acid strongly increases and the ratio of concentration of acetic acid to formic acid at 60 days is higher than 5.5. These results indicate that under accelerated ageing, commercial wood-containing paper in bags, at 98°C and 50 % RH, a steady-state growth of the mentioned acid concentration occurs during the first days of the ageing. The acetic acid to formic acid molar ratio is ranging from 1.4 to 2.0 within the first 10 days of ageing. Subsequently, probably there is a change of the ageing mechanism and the share of acetic acid increases. One of the reasons of this phenomenon may lie in a possible oxidation of the previously formed cellulose fragments leading predominantly to acetic acid formation. An alternative explanation is based on the absorption of formed volatile acids products of paper degradation, which accelerated their ageing (autocatalysis) in the bags. This mode of acetic acid formation was supported by the work Shahani and Harrison (2002), which shown that in the sealed tube, the organic compounds produced during the degradation remain in contact with the paper during the entire ageing period (as in a closed book) and are believed to accelerate the degradation rate. In the previous work (Dupont et al. 2007) it has been shown that the production of acids, and sum of formate and acetate showed a linear progression at accelerated ageing to 8 days inside hermetically sealed glass tubes in a dry heat oven at 100°C. These two acids are useful as indicators of paper degradation. The production of acetic acid in paper as an indicator of the evolution of the degradation has been proposed earlier (Ligterink and Pedersoli 2001).

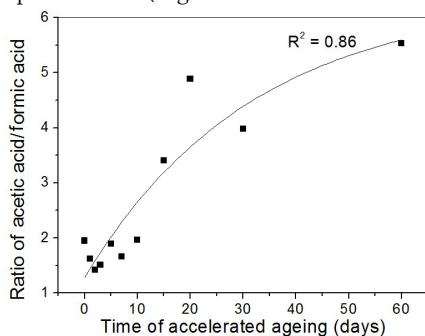


Fig. 5: Relationship between accelerated ageing at temperature 98°C, 50 % RH. and ratio of acetic/formic acid.

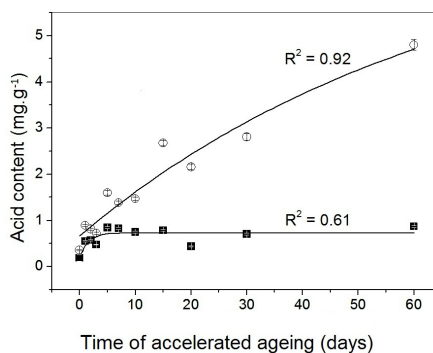


Fig. 6: Influence of accelerated ageing at temperature 98°C, 50 % RH on the content of acetic and formic acid.
 ■ – concentration of formic acid ($\text{mg}\cdot\text{g}^{-1}$)
 ○ – concentration of acetic acid ($\text{mg}\cdot\text{g}^{-1}$)

It is apparent that the acetic or formic acid content has approximately exponential relationship with the time of accelerated ageing (Fig. 6). Results presented in Fig. 6 confirmed the significance of acid content during the ageing as an exponential correlation is obtained between content of acetic acid and formic acid and the time of accelerated ageing at 98°C. The prolonged time of

ageing increases the formation of acetic acid in aged paper and this behaviour is described by relation $C_{AA} = 7.446 - 6.783.e^{(-0.015.t)}$. Formation of formic acid in aged paper can be described by the equation $C_{FA} = 0.732 - 0.521.e^{(-0.632.t)}$ (Jablonský et al. 2011b). In the previous two equations is "t" parameter meant as time expressed by the number of days of accelerated ageing at 98°C and RH 50 %. The correlation coefficients, R^2 , were 0.94 for the concentration of acetic acid and 0.61 for the concentration of formic acid. The concentration of formic acid increased just in the first stages of the ageing (to 5 days at accelerated ageing at 98°C), afterwards it is kept constant.

Formic acid concentration increased with accelerated time at 98°C and 50 % RH during the first 5 days. Before initiation of their ageing, $C_{FA} = 0.185 \text{ mg} \cdot \text{g}^{-1}$ paper and after 5 days ageing it reaches $C_{FA} = 0.844 \text{ mg} \cdot \text{g}^{-1}$ paper. After that, the rate of release of formic acid was very low, but the concentration was not decreased. The concentration of formic acid afterwards is kept constant in the range of times of accelerated ageing from 5 to 60 days. In case of acetic acid, its concentration gradually increases from the initial $0.361 \text{ mg} \cdot \text{g}^{-1}$ paper to $4.798 \text{ mg} \cdot \text{g}^{-1}$ paper after 60 days of ageing. This observation complies with the conclusion accepted by various authors (Lattuati-Derieux et al. 2006, Dupont et al. 2007, Pedersoli et al. 2011), that acetic acid may act as a general marker of degradation.

The acidic products formed during the accelerated ageing accumulate inside the paper and inter-sheet spaces of books or archival files, resulting in enhanced degradation (Bansa 1998). This means that a stack of sheets degrades faster than a single sheet. Hanus et al. (1996) have shown that the degradation rate inside a paper stack is higher than in the top and bottom of the sheets. During the experiment done by Carter et al. (2000) the degradation products of accelerated ageing at 90°C could only migrate in a stack in one direction and evaporate into the surrounding air from the top of the stack. Thus, the concentration of acids in the top pages was smaller. In a follow-up study it was found that this topochemical effect decreased with temperature; it may be supposed that at room temperature, i.e. during natural ageing, it is of minor importance (Bulow et al. 2000). The degradation of cellulose at low temperature can come from oxidation/ or acid-catalysed hydrolysis. According by Zou et al. (1994) the loss of fibre strength is, in turn, due to depolymerization of the cellulose caused by acid-catalysed hydrolysis. The influence of acid concentration (summary acetic and formic acid, concentration of individual acids: acetic and formic acid) generated in paper during the accelerated of ageing has increased the strength loss is shown in Fig. 7. Results of recent study Jablonský et al. (2011a, b) suggest that the brittleness of aged paper was more dependent on concentration of acetic acid than formic acid. Taking into account that brittleness index of papers were calculated by strength curves, correlation between tensile strength and formed light acids can be expected. Curves are drawn for easier visualization of the trends in the data: these were generated by linear regression. There was a significant inverse correlation between the tensile strength and summary content of acetic and formic acid ($r = -0.949$); for concentration of acetic acid ($r = -0.959$); for concentration of formic acid ($r = -0.520$). Although between tensile strength and formic acid were not significantly correlated ($R^2 = 0.27$). Given that the linear regression fits displays R^2 -values of 0.9 for summary acid; and 0.92 for acetic acid, it can be concluded that correlate strongly with them. The loss of fibre strength due to degradation correlates well with the increase of the $\text{CH}_3\text{COOH}/\text{HCOOH}$ ratio as well. The correlation coefficients of the linear regression of $R^2 = 0.84$ is shown in Fig. 8.

Thus evidence suggests that the acid-catalysed hydrolysis or oxidation causes mainly formation of acetic and the contribution of the amount of the formic acid is marginal. These acids apparently cause the cellulose degradation which is presented as a loss of strength. The hydrolysis rates of polysaccharides are faster in acidic media than in neutral and alkaline media (Sundqvist 2004). Very important factor in the case of acceleration of the paper degradation is higher amount

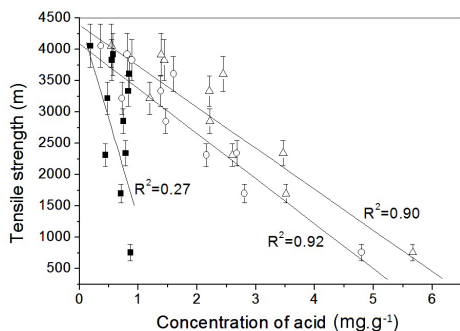


Fig. 7: Tensile strength vs. concentration of acid. The accelerated ageing at temperature 98°C and 50 % RH.

■ – concentration of formic acid ($\text{mg}\cdot\text{g}^{-1}$)

○ – concentration of acetic acid ($\text{mg}\cdot\text{g}^{-1}$)

△ – summary concentration of acetic and formic acid ($\text{mg}\cdot\text{g}^{-1}$)

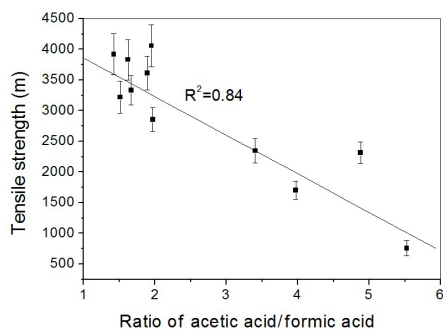


Fig. 8: Relationship between tensile strength and ratio of acetic acid/formic acid at accelerated ageing at 98°C and 50 % RH.

of acetic acid. Formation of formic acid is gentle with longer period of accelerated ageing. It was found that the ratio of acetic/formic acid content is 2, when the accelerated ageing was carried out up to 10 days at temperature 98°C. At longer time period of accelerated ageing formation of acetic acid strongly increases and ratio of acetic/formic acid and at 60 days is higher than 5.5. This indicates that during the accelerated ageing the formation of acetic acid mainly causes loss of strength. The correlation between mechanical properties (folding endurance, brittleness index (Jablonský et al. 2011b, 2012) and tensile strength) and formation of acids could be critical for a predictive understanding of the role of degradation/deterioration of cultural heritage on the paper carriers and materials.

CONCLUSIONS

The investigation of the influence of accelerated ageing at temperature 98°C, RH 50 % upon the generated acetic and formic acid, strength loss (tensile strength) and surface/or cold extract pH can be summarized as follows:

- With longer period of accelerated ageing the surface/or cold extract pH and tensile strength decrease.
- During the first 5 days of the prolongation of time of accelerated ageing, acetic acid concentration increases. After that the rate of release of formic acid was low, but the concentration did not decrease. The magnitude of strength loss was found to be affected by the concentration of the acetic acid.
- The ratio of acetic acid to formic acid concentration in situ increases during the accelerated ageing 2 times $\text{CH}_3\text{COOH}/\text{HCOOH}$ after 10 days and 5.5 after 60 days.
- The loss of fibre strength due to degradation correlates well with the increase of acetic acid concentration in situ and the $\text{CH}_3\text{COOH}/\text{HCOOH}$ ratio as well.

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