3rd International Conference on Integrated Information (IC-ININFO)

Experimental design for the investigation of the environmental factors effects on organic materials (Project INVENVORG). The case of paper.

Spiros Zervos[a], Konstantinos Choulis[b] and Georgios Panagiaris[b]

[a]*Technological Educational Institute of Athens, Department of Library Science and Information Systems*
[b]*Technological Educational Institute of Athens, Department of Conservation of Antiquities & Works of Art*

Abstract

In this paper, we first outline the Thales EC-supported project INVENVORG, which investigates the effects of the environmental factors on non-treated organic materials, namely bone, woolen textile, parchment, paper and wood. The project planning includes an accelerated ageing study (with exposure to elevated temperatures and relative humidities, light and pollutants) and then a natural ageing study in monitored museums environments, followed by the statistical correlation analysis of the material properties after accelerated and natural ageing with the environmental stresses, in order to determine the real life relative contribution of the various environmental parameters to material ageing.
After a literature review concerning the exhaustive research on the accelerated ageing of paper, the experimental design pertaining to paper is presented. Accelerated ageing will be used for the production of artificially aged samples that emulate aged paper in a controlled manner. A preliminary ageing experiment will help determine the most suitable conditions, and will provide data that will be correlated to those produced by natural ageing. Virgin and artificially aged samples will then be exposed for 2 years to closely monitored museums environments. Tearing strength, degree of polymerization determined by viscometry, pH and the color coordinates of the CIEL*a*b* colour system will be determined and used for the statistical analysis.

Selection and peer-review under responsibility of the 3rd International Conference on Integrated Information.

INVENVORG; paper; accelerated ageing; natural ageing; experimental setup

---

1. Introduction: The INVENVORG Project

This paper presents the experimental design pertaining to paper, in the framework of the Thales EC-supported project INVENVORG. Project INVENVORG was launched in the beginning of 2012 and investigates the effects of the environmental factors on the major representatives of non-treated organic materials, namely bone (representative of hard tissue proteinaceous materials), woolen textile (keratinous composition), parchment (collageneous material), paper and wood (cellulosic and cellulose-lignin structure). These materials constitute the major ingredients of most objects stored in natural history and folk-ethnographic museums, libraries and archives but also of many artefacts kept in historical and archaeological museums and are decaying at a fast rate.

As stated verbatim in the project proposal: *Amongst the materials constituting Cultural Heritage, organic materials of animal origin (proteinaceous materials such as bone, antler, horn, ivory, leather, parchment, woolen textiles, silk etc.) as well as of plant origin (cellulosic or lignocellulosic eg. wood, paper, straw, cotton or linen textile etc.) are the most susceptible to damage and decay due to their exposure to biotic and abiotic factors. Air pollution, inappropriate values and fluctuations of ambient temperature and humidity, light and microorganisms in museums, favor the complete decomposition of these materials. Most prone to decay are the organic materials that have not been treated in a way to enhance their resistance to decay caused by environmental factors. Therefore within the museum community it is critical to define and to achieve the most suitable environmental conditions for the preventive conservation of these materials either in storage, display and/or in transit. Non-treated organic materials constitute a great proportion -if not the majority- of the manufacturing materials of artefacts in folk-ethnographic museums, natural history museums, libraries-archives as well as in historical and archaeological museums. Furthermore, these kind of organic materials exist as component-structural materials of artefacts hosted in modern art collections or other types of museums.*

The major target of the project is to study the contribution and the effects of the various environmental factors on the artificial and natural ageing of the above mentioned materials. To that end, during the first phase of the project, samples of these materials will be subjected to artificial ageing under various setups utilizing the most important stress factors found in the literature. In the second phase, the samples will be exposed to real monitored museum environments for various time intervals and will then be analyzed by the same methods used for the characterization of the virgin and artificially aged samples. Statistical methods will be used to correlate decay factors with the extent and type of damage.

The project enhances inter-disciplinarity and trans-disciplinarity focusing less on scientific disciplines and more on research domains according to the recommendation of the Commission of the European Communities as expressed in the "Communication from the Commission to the Council and the European Parliament – Delivering on the modernization agenda for Universities: Education, Research and Innovation" [Brussels, 10/05/2006, COM (2006), 208 final].

In order to achieve the goals of the project, there will be close collaboration between all the research teams brought together from various academic/research institutes across Greece and Denmark:

Research Team 1:

- Technological Educational Institute of Athens (TEI-A) - Department of Conservation of Antiquities and Works of Art (DCAWA), Organic Materials Conservation Laboratory and Physicochemical Diagnostic and Documentation Methods Laboratory
- Danish Royal Academy of Fine Arts (DRAFA), School of Conservation, Object Conservation Laboratory
- TEI of Piraeus - Department of Textile (TEI-P), Textile Fibers Laboratory

Research Team 2:

- National Technical University of Athens - Department of Mechanics (NTUA), Strength Test Laboratory
- Clothing Textile & Fibre Technology Development Company (CLOTEFI), Testing Laboratories

Research Team 3:

- Foundation for Research and Technology of Patras - Institute of Chemical Engineering and High Temperature Chemical Processes (FORTH/ICE-HT), Applied Molecular Spectroscopy Laboratory
- University of Patras - Department of Chemical Engineering (UoP), Lab8: Physical Chemistry and High Temperature Spectroscopy Laboratory

Research Team 4:

- University of Ioannina - Department of Chemistry (UoI), Peptide Chemistry Laboratory

  Research Team 5:
- Technical University of Crete - Department of Environmental Engineering (TUoC), Atmospheric Aerosols Laboratory

  Research Team 6:
- Athens University of Economics and Business – Department of Statistics (AUEB), Statistical methodology and data analysis Laboratory

The research teams are representative active members of the state-of-the-art in the respective fields. The project aims at developing stronger links among European researchers by inviting the researcher from the Danish Royal Academy of Fine Arts (DRAFA), School of Conservation. This aim is crucial to the building of the European Research Area (ERA) and to the strengthening of the foundations of scientific excellence across Europe.

2. Literature Review

Of all the materials stored in museums, archives and libraries, paper is the most extensively studied, mainly because of its importance as a ubiquitous industrial material. There exist numerous studies concerning the impact of the environment on the ageing of paper which have been critically reviewed in several publications (Feller et al. 1986; Fellers et al. 1989; Emsley & Stevens 1994; Feller 1994; Shahani et al. 2001; Zervos 2010; Area & Cheradame 2011). The most important of them are collectively presented below, organized by their objectives and findings. These studies:

- Report on, elucidate and correlate with the conditions of ageing the mechanisms that are responsible for the accelerated ageing of paper (Feller et al. 1986; Fellers et al. 1989; Emsley & Stevens 1994; Feller 1994; Zou et al. 1994; Zou et al. 1996a; Shahani et al. 2001; Barański et al. 2004a; Barański et al. 2004b; Calvini 2005; Barański et al. 2006; Calvini et al. 2008; Stephens et al. 2008; Stephens et al. 2010).
- Propose kinetic models that correlate the rate of degradation with temperature, relative humidity, paper acidity, paper additives concentration, atmosphere composition etc. (Graminski et al. 1979; Shafizadeh & Bradbury 1979; Erhardt et al. 1987a; Erhardt 1989; Erhardt 1993; Zou et al. 1993; Zou et al. 1994; Zou et al. 1996a; Barański et al. 2004a; Barański et al. 2004c; Stephens et al. 2008).
- Report on the effects of the urban atmospheric pollutants (SO2, NOχ και O3) on the rate of ageing (Daniel et al. 1990; Herrera 1990; Havermans 1995; Daniel 1996; Begin et al. 1999; Reilly et al. 2000; Proniewicz et al. 2001; ASTM D 6833-02 2002).
- Report on the effects of light and ionizing radiation on the stability and ageing of paper (Hon 1981; Wilson & Parks 1983; Feller et al. 1986; Lee & Feller 1986; Lee et al. 1989; Andrady et al. 1991; Leclerc & Flieder 1992; Bailey & Lamont 1993; Heitner 1996; Havermans & Dufour 1997; Adamo et al. 1998; Bukovsky 2000a; Bukovsky 2000b; Forsskåhl 2000; ASTM D 6789-02 2002; Bukovsky & Trnkova 2003)
- Propose and standardize various paper accelerated ageing protocols (ISO 5630-2 1985; ISO 5630-1 1991; ISO 5630-3 1996; Bansa 2002). Specifically, in 2002 a protocol was proposed and standardized for ageing in sealed vessels, which was proved to simulate natural ageing better than the previous ones (Shahani et al. 2001; Begin & Kaminska 2002).
- Have identified the products of natural and accelerated ageing of paper, and to a certain degree have correlated them and their concentrations with the conditions of ageing (Erhardt et al. 1987b; Erhardt et al. 1999; Shahani et al. 2001; Lattuati-Derieux et al. 2006; Strlič et al. 2007; Strlič et al. 2009; Stephens et al. 2010).
- Propose various techniques for the estimation of the service life of paper, based on accelerated ageing and the use of Arrhenius studies (Bansa & Hofer 1989; Strofer-Hua 1990; Emsley & Stevens 1994; Zou et al. 1996a; Zou et al. 1996b; Shahani et al. 2001; Ding & Wang 2007; Zervos 2010).
- Have investigated and propose the most efficient methods for the characterization of paper and for the quantification of the results of paper ageing (Shahani 1995; Shahani et al. 2001; Strlič et al. 2005; Zervos & Moropoulou 2006; Strlič et al. 2007; Zervos 2007b; Lichtblau et al. 2008; Strlič et al. 2009).

Most of these studies include the exposure of samples of various types of contemporary and historic paper to controlled atmospheres inside ageing chambers, that is, the use of accelerated ageing. The temperatures used range from ambient up to 1000°C, usually between 70 to 100°C (Emsley & Stevens

1994; Shahani et al. 2001; Zervos 2010). These experiments have utilized the full range of all possible combinations of temperatures and relative humidities. The cycling of relative humidity and temperature has also been studied (Shahani et al. 1989; Bigourdan & Reilly 2002).

3. Paper Ageing Experimental Design

For the above mentioned reasons, the study of paper ageing was excluded from the first stage of this project. A new study of the accelerated ageing of paper in the framework of this project's design and objectives was considered redundant, since it would have added considerably to the cost but would have not produced new knowledge. Contrariwise, there are very few studies of the natural ageing of paper, and most of them concern ageing in non-monitored environments (Wilson et al. 1955; Wilson & Parks 1980; Wilson & Parks 1983; Zervos 2010).

Nevertheless, two accelerated ageing experiment are planned, with the following objectives: The first - which is underway - is a multi-withdrawal, single temperature and relative humidity experiment, which will help determine the overall degradation behavior of the samples, that is, the dependence of the extent of degradation on the duration of ageing. The results of the first experiment will be used for the determination of the optimum duration for the second ageing experiment, which has as a single objective the production of samples that emulate aged paper in a controlled manner (Sclawy 1981; Porck 2000; Calvini & Gorassini 2002b; Calvini & Gorassini 2002a; Zervos 2007b).

Concerning the choice of paper samples, it was decided that pure cellulose paper should be studied, since it would represent the simplest possible chemical system. The existence of additives, lignin and other components of commercial paper may introduce many unknown factors and would add to the complexity of the system, making very difficult or even impossible to determine and isolate trends. Thus, Whatman no 2 filter paper was used for the preparation of samples, a standard paper with repeatable properties which has been extensively studied and widely used to model pure cellulose paper, since it comprises pure cotton with no additives, fillers or sizing (Daniels 1976; Moropoulou & Zervos 2003; Zervos & Moropoulou 2005; Zervos 2007b). An industrial historic alum/rosin-sized lignin containing paper, similar to historic paper stored in museums, libraries and archives will also be used in its virgin state in the second phase.

It has been shown that ageing paper at medium to relatively high humidity levels (50-80%) and at temperatures around 80-90°C, simulates natural ageing sufficiently well (Erhardt & Mecklenburg 1995). Both accelerated ageing experiments are planned to be performed at 90°C and 78% RH in sealed vessels (adaptation of ASTM D 6819-02 2002 ageing standard). The RH inside the sealed vessels can be set at 78% by use of saturated NaCl solutions (Greenspan 1977). Although we initially opted for 80°C, time restrictions called for higher temperatures. 90°C lies well within the acceptable temperature range and does not induce degradation reactions irrelevant to natural paper ageing (Erhardt & Mecklenburg 1995). The 10 degrees temperature increase should speed up the ageing reaction by a factor of 2 - 4, since according to the relevant literature a rise of 5 – 10 degrees doubles the speed of the reaction (Zervos 2010).

In previously published papers (Zervos & Moropoulou 2005; Zervos 2007a), we presented the study of the accelerated ageing of the same paper (Whatman no 2) at nearly the same RH (75%), but at a lower temperature (80°C). Results of these studies, presenting the ageing profile of Whatman no 2 paper, as determined by following various properties during ageing, can be seen in fig. 1. This experiment lasted up to 150 days, when all usability was lost, as indicated by the zeroing of folding endurance, with 4 intermediate withdrawals. In order to duplicate this ageing profile at 90°C, and after taking into consideration the rule of thumb presented above about the temperature dependence of paper degradation, we decided that ageing should last for at least 50 days, with withdrawals every 10 days. For the determination of the "optimum" duration of ageing for the preparation of aged samples that will be used in the second phase, the two graphs at the bottom of fig. 1 were considered. These graphs show two of the mechanical properties of Whatman paper, namely folding endurance and tensile strength, and indicate that there is a turning point between 90 and 120 days of ageing, where the decline of the properties accelerates. Our target is to age paper up to that point, which will be determined from the ageing profile created at 90°C. Thus, paper will be sensitized towards ageing and there is a good chance that the aged samples will show property changes after the exposure to the museums environments (Feller 1977; Feller et al. 1986; Feller 1994).

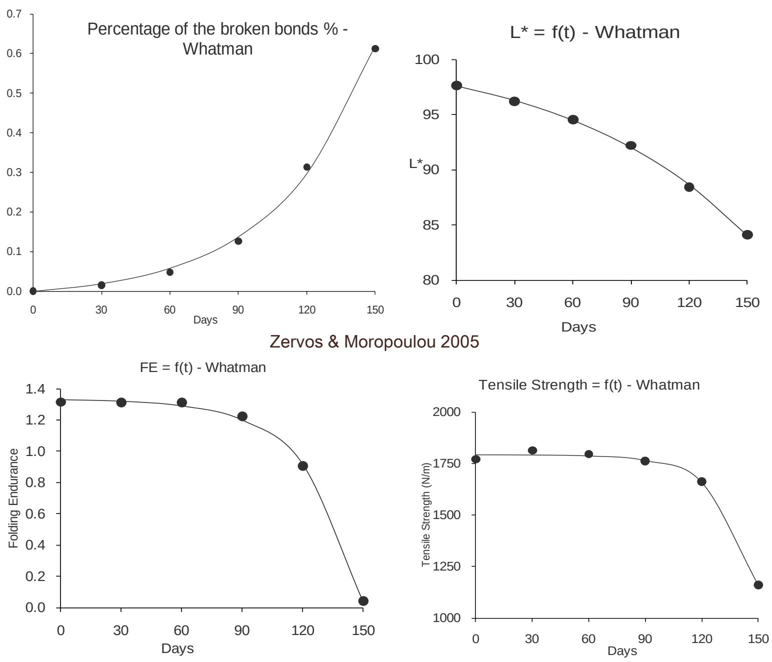

Fig. 1. Ageing profiles of Whatman no 2 paper, as determined by following various properties during ageing at 80°C and 75% in sealed vessels (Zervos & Moropoulou 2005; Zervos 2007a).

In the second phase of the project, virgin and artificially aged samples prepared in the first phase will be exposed to real museums environment to undergo natural ageing. The study of natural paper ageing in real typical museum environments is extremely useful, provided that the environmental conditions would be closely monitored. Such a study would offer valuable insight into the real life relative contribution of the various environmental parameters (temperature, relative humidity, light, gaseous pollutants) to paper ageing. For these reasons, paper samples will be included in the second phase of this study, that is, the exposure of paper samples to real monitored museum environments. The samples will include virgin and artificially aged paper that will be examined by the same methods used for the characterization of the naturally aged samples. According to the project proposal, there will be one sample withdrawal near the end of the project, so that the natural ageing will last for 2 years. The samples will then be characterized and their properties will be compared to those of the virgin and the artificially aged samples. A rigorous statistical study of the results will hopefully reveal the relative contribution of the various degradation factors on the overall deterioration. In addition, one full set of paper samples will be left in the museums for future studying, after the end of the INVENVORG project.

According to the planning of the project, the properties showed in the following table (table 1) will be determined. These properties are considered as the basic representatives of the chemical, mechanical and optical properties of paper and are recommended in several studies as the most sensitive to ageing (Zervos & Moropoulou 2006; Zervos 2010). The table indicates the relevant standards for the properties determination and an estimation of the variability of each property derived from the indicated literature.

Table 1. Properties that will be determined for the characterization of the samples.

Property	Standard	Standard Deviation
Degree of Polymerization by viscometry	(ASTM D 1795-96 R2001)	Less than 1.1% (Zervos 2007)
pH of the cold extract of paper or by contact electrode	(ISO 6588 1981)	Around 1.3% and for aged samples never exceeded 2.2% (Zervos 2007)
Tearing resistance (Elmendorf method)	(ISO 1974 1990)	Repeatability about 3.5% (ISO 1974 1990)
Color (CIEL*a*b* color space): L* and b* coordinates	(ASTM D 2244-93 1993)	L* less 1% - b* between 4% and 6% (Zervos 2007)

The number of the repetitions per measurement is stated in the relevant standards. Experience and literature indicate that paper is a highly inhomogeneous material. Thus, randomization of the samples is of utmost importance. Whenever cost is not an issue, it is also considered good practice to repeat a measurement until all the available sample is depleted, compensating thus for the inhomogeneity of the material and increasing the precision of the measurement (Zervos 2007b).

Acknowledgements

This research has been co-financed by the European Union (European Social Fund – ESF) and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) - Research Funding Program: THALES. Reinforcement of the interdisciplinary and/or inter-institutional research and innovation with the possibility of attracting high standard researchers from abroad through the implementation of basic and applied excellence research.

References

Adamo, M, Giovannotti, M, Magaudda, G, Zappala, MP, Rocchetti, F & Rossi, G (1998). *Effect of gamma rays on pure cellulose paper as a model for the study of a treatment of biological recovery of biodeteriorated books*. Restaurator 19(1): 41-59.

Andrady, AL, Song, Y, Parthasarathy, R, Fueki, K & Torikai, A (1991). *Photoyellowing of mechanical pulp. Part 1: Examining the wavelength sensitivity of light-induced yellowing using monochromatic radiation*. TAPPI Journal 74(8): 162-168.

Area, MC & Cheradame, H (2011). *Paper Aging and Degradation: Recent Findings and Research Methods*. BioResources 6(4): 5307-5337.

ASTM D 1795-96 (R2001). *Standard test method for intrinsic viscosity of cellulose*.

ASTM D 2244-93 (1993). Standard test method for calculation of color differences from instrumentally measured color coordinates.

ASTM D 6789-02 (2002). Test method for accelerated light aging of printing and writing paper by xenon-arc exposure apparatus.

ASTM D 6833-02 (2002). Test method for accelerated pollutant aging of printing and writing paper by pollution chamber exposure apparatus

Bailey, AL & Lamont, LJ (1993). *A standard procedure for accelerated testing and measurement of yellowing by light in papers containing lignin*. TAPPI Journal 76(09): 175-180.

Bansa, H (2002). *Accelerated ageing of paper: Some ideas on its practical benefit*. Restaurator 23(2): 106-117.

Bansa, H & Hofer, HH (1989). *Artificial ageing as a predictor of paper's future useful life*. Abbey Newsletter Supplement 1.

Barański, A, Dutka, D, Dziembaj, R, Konieczna-Molenda, A & Lagan, JM (2004a). *Effect of relative humidity on the degradation rate of cellulose. Methodology studies*. Restaurator 25(1): 68-74.

Barański, A, Łagan, JM & Łojewski, T (2004b). The concept of mixed-control mechanisms and its applicability to paper degradation studies. In: Kolar, J, Strlic, M & Havermans, J (eds.) Proceedings of the international conference: Durability of paper and writing, Ljubljana, Slovenia. National and University Library: 35-36.

Barański, A, Łagan, JM & Łojewski, T (2006) "The concept of mixed-control mechanisms and its applicability to paper degradation studies." e-Preservation Science 3, 1-4

Barański, A, Łagan, JM, Łojewski, T & Sawoszczuk, T (2004c). Experimental verification of Zou, Uesaka and Gurnagul formalism, based on kinetic data obtained for various kinds of paper. In: Kolar, J, Strlic, M & Havermans, J (eds.) Proceedings of the international conference: Durability of paper and writing, Ljubljana, Slovenia. National and University Library: 76-77.

Begin, P, Deschatelets, S, Grattan, D, Gurnagul, N, Iraci, J, Kaminska, E, Woods, D & Zou, X (1999). *The effect of air pollutants on paper stability*. Restaurator 20(1): 1-21.

Begin, PL & Kaminska, E (2002). *Thermal accelerated ageing test method development*. Restaurator 23(2): 89-105.

Bigourdan, J & Reilly, J (2002). Effects of fluctuating environments on paper materials — stability and practical significance for preservation. La Conservation à l'Ère du Numérique, Actes des Quatrièmes Journées Internationales d'Études de l'ARSAG, Paris. Association pour la Recherche Scientifique sur les Arts Graphiques: 180-192.

Bukovsky, V (2000a). *The influence of light on aging of newsprint paper*. Restaurator 21(2): 55-76.

Bukovsky, V (2000b). *The natural ageing of paper after exposure to daylight*. Restaurator 21(4): 229-237.

Bukovsky, V & Trnkova, M (2003). *The influence of secondary chromophores on the light induced oxidation of paper. Part II: The influence of light on groundwood paper*. Restaurator 24(2): 118-132.

Calvini, P (2005). *The influence of the leveling-off degree of polymerization on the kinetics of cellulose degradation*. Cellulose 12: 445–447.

Calvini, P & Gorassini, A (2002a). *The degrading action of iron and copper on paper. A FTIR-deconvolution analysis*. Restaurator 23(4): 205-221.

Calvini, P & Gorassini, A (2002b). *FTIR - deconvolution spectra of paper documents*. Restaurator 23(1): 48-66.

Calvini, P, Gorassini, A & Merlani, L (2008). *On the kinetics of cellulose degradation: looking beyond the pseudo order rate equation*. Cellulose 15: 193–203.

Daniel, F (1996). *A pollution chamber for the accelerated deterioration of materials*. Restaurator 17(3): 193-202.

Daniel, F, Flieder, F & Leclerc, F (1990). *The effects of pollution on deacidified paper*. Restaurator 11(3): 179-207.

Daniels, V (1976). *The elimination of bleaching agents from paper*. The Paper Conservator 1: 9-11.

Ding, H-Z & Wang, ZD (2007). *Time–temperature superposition method for predicting the permanence of paper by extrapolating accelerated ageing data to ambient conditions*. Cellulose 14(3): 171–181.

Emsley, AM & Stevens, GC (1994). *Kinetics and mechanisms of the low-temperature degradation of cellulose*. Cellulose 1: 26-56.

Erhardt, D (1989). *Relation of reaction rates to temperature*. The Abbey Newsletter 13(3): 38-39.

Erhardt, D (1993). Temperature and relative humidity effects on the aging of cellulose. In: Beyer, C (ed.) Preservation research and development. Round table proceedings. Library of Congress Preservation Directorate: 31-34.

Erhardt, D, Endt, DV & Hopwood, W (1987a). The comparison of accelerated aging conditions through the analysis of artificially aged paper. Preprints of papers presented at the fifteenth annual meeting, Vancouver, Canada. American Institute for Conservation: 43-55.

Erhardt, D & Mecklenburg, MF (1995). Accelerated vs natural aging: Effect of aging conditions on the aging process of cellulose. In: Vandiver, PB, Druzik, JR, Madrid, JLG, Freestone, IC & Wheeler, GS (eds.) Materials issues in art and archeology IV, Cancun, Materials Research Society Symposium Proceedings. Materials Research Society, 352: 247-270.

Erhardt, D, Tumosa, CS & Mecklenburg, MF (1999). Meterial consequences of the ageing of paper. In: Bridgland, J (ed.) 12th Triennial Meeting, Lyon. ICOM-CC, vol. 2: 501-6.

Erhardt, D, Von Endt, D & Hopwood, W (1987b). The comparison of artificial aging conditions through the analysis of extracts of artificially aged paper. In: Brown, AJ (ed.) 15th Annual Meeting of AIC, Vancouver, British Columbia, Canada 43-55.

Feller, RL (1977). Stages in the deterioration of organic materials. In: Williams, JC (ed.) Preservation of paper and textiles of historic and artistic value. Advances in Chemistry Series 164. Washington, DC, American Chemical Society, pp. 314-335.

Feller, RL (1994). Accelerated Aging: Photochemical and Thermal Aspects. Marina del Rey, The Getty Conservation Institute.

Feller, RL, Lee, SB & Bogaard, J (1986). The kinetics of cellulose deterioration. In: Needles, HL & Zeronian, SH (eds.) Historic textile and paper materials. Conservation and characterization. Advances in Chemistry Series 212. Washington, DC, American Chemical Society, pp. 329-347.

Fellers, C, Iversen, T, Lindstrom, T, Nilsson, T & Rigdahl, M (1989). Ageing/degradation of paper, a literature survey. FoU-projektet for papperskonservering. Stockholm, FoU-projektet for papperskonservering.

Forsskåhl, I (2000). Light aging test method development: ASTM research program into the effect of aging on printing and writing papers, Finnish Pulp & Paper Research Institute (KCL).

Graminski, EL, Parks, EJ & Toth, EE (1979). The effects of temperature and moisture on the accelarated ageing of paper. In: Eby, RK (ed.) Durability of macromolecular materials. ACS Symposium Series 95. Washington, DC, American Chemical Society, pp. 341-355.

Greenspan, L (1977). *Humidity fixed points of binary saturated aqueous solutions*. Journal of research of the National Bureau of Standards. A, Physics and chemistry 81A(1): 89-96.

Havermans, JBGA (1995). *Effects of air pollutants on the accelerated aging of cellulose-based materials*. Restaurator 16(4): 209-233.

Havermans, JBGA & Dufour, J (1997). *Photo oxidation of paper documents - A literature review*. Restaurator 18(3): 103-114.

Heitner, C (1996). Chemistry of brightness reversion and its control. In: Dence, C & Reeve, D (eds.) Pulp bleaching, principles and practice. Atlanta, GA, Tappi Press, pp. 185-212.

Herrera, M (1990). *Analysis of ozone concentration and its influence on the archives of the Kingdom of Aragon, Barcelona*. Restaurator 11(3): 208-216.

Hon, DN-S (1981). Yellowing of modern papers. In: Williams, JC (ed.) Preservation of paper and textiles of historic and artistic value II. Advances in Chemistry Series 193. Washington, DC, American Chemical Society, pp. 119-142.

ISO 1974 (1990). Paper - Determination of tearing resistance (Elmendorf method).

ISO 5630-1 (1991). Paper and board - Accelerated ageing. Part 1: Dry heat treatment at 105 ºC.

ISO 5630-2 (1985). Paper and board - Accelerated ageing. Part 2: Moist heat treatment at 90 ºC and 25% relative humidity.

ISO 5630-3 (1996). Paper and board - Accelerated ageing. Part 3: Moist heat treatment at 80 ºC and 65% relative humidity.

ISO 6588 (1981). Paper, board and pulps - Determination of pH of aqueous extracts.

Lattuati-Derieux, A, Bonnassies-Termes, S & Lavédrine, B (2006). *Characterisation of compounds emitted during natural and artificial ageing of a book. Use of headspace-solid-phase microextraction/gas chromatography/mass spectrometry*. Journal of Cultural Heritage 7 123–133.

Leclerc, F & Flieder, F (1992). Influence of optical brighteners on paper permanence. Conference Papers, Manchester, Institute of Paper Conservation: 257-263.

Lee, SB, Bogaard, J & Feller, RL (1989). Damaging effects of visible and near-ultraviolet radiation on paper. In: Zeronian, SH & Needles, HL (eds.) Historic textile and paper materials II. Conservation and characterization. ACS Symposium Series 410. Washington, DC, American Chemical Society, pp. 54-62.

Lee, SB & Feller, RL (1986). Influence of the hemicellulose fraction on thermal and photochemical discoloration of paper. In: Needles, HL & Zeronian, SH (eds.) Historic textile and paper materials. Conservation and characterization. Advances in Chemistry Series 212. Washington, DC, American Chemical Society, pp. 377-386.

Lichtblau, D, Strlič, M, Trafela, T, Kolar, J & Anders, M (2008). *Determination of mechanical properties of historical paper based on NIR spectroscopy and chemometrics - a new instrument* Applied Physics A 92(1): 191-195.

Moropoulou, A & Zervos, S (2003). *The immediate impact of aqueous treatments on the strength of paper*. Restaurator 24(3): 160-177.

Porck, H (2000). Rate of paper degradation. The predictive value of artificial aging tests, European Commission on Preservation and Access, Amsterdam.

Proniewicz, LM, Paluszkiewicz, C, Weselucha-Birczynska, A, Majcherczyk, H, Baranski, A & Konieczna, A (2001). *FT-IR and FT-Raman study of hydrothermally degradated cellulose*. Journal of Molecular Structure 596: 163-169.

Reilly, JM, Zinn, E & Adelstein, P (2000). Atmospheric pollutant aging test method development: Report to ASTM, Image Permanence Institute at Rochester Institute of Technology (IPI).

Sclawy, AC (1981). The effect of varying relative humidity conditions on the folding endurance of aged paper samples. In: Williams, JC (ed.) Preservation of paper and textiles of historic and artistic value II. Advances in Chemistry Series 193. Washington, DC, American Chemical Society, pp. 217-222.

Shafizadeh, F & Bradbury, AGW (1979). *Thermal degradation of cellulose in air and nitrogen at low temperatures*. Journal of Applied Polymer Science 23: 1431-1442.

Shahani, C, Lee, SB, Hengemihle, FH, Harrison, G, Song, P, Sierra, ML, Ryan, CC & Weberg, N (2001). Accelerated aging of paper: I. Chemical analysis of degradation products. II. Application of Arrhenius relationship. III. Proposal for a new accelerated aging test: ASTM research program into the effect of aging on printing and writing papers. Washington, DC, Library of Congress.

Shahani, CJ (1995) "Accelerated aging of paper: Can it really foretell the permanence of paper." Preservation Research and Testing Series 9503,

Shahani, CJ, Hengemihle, FH & Weberg, N (1989). The effect of variations in relative humidity on the accelerated aging of paper. In: Zeronian, SH & Needles, HL (eds.) Historic textile and paper materials II. Conservation and characterization. ACS Symposium Series 410. Washington, DC, American Chemical Society, pp. 63-80.

Stephens, CH, Shrestha, B, Morris, HR, Bier, ME, Whitmore, PM & Vertes, A (2010). *Minimally invasive monitoring of*

cellulose degradation by desorption electrospray ionization and laser ablation electrospray ionization mass spectrometry. Analyst 135(9): 2434-2444.
Stephens, CH, Whitmore, PM, Morris, HR & Bier, ME (2008). *Hydrolysis of the amorphous cellulose in cotton-based paper*. Biomacromolecules 9(4): 1093-9.
Strlič, M, Cigić, IK, Kolar, J, De Bruin, G & Pihlar, B (2007). *Non-destructive evaluation of historical paper based on pH estimation from VOC emissions*. Sensors 7: 3136-3145.
Strlič, M, Kolar, J & Pihlar, B (2005). Methodology and analytical techniques in paper stability studies. In: Strlič, M & Kolar, J (eds.) Ageing and stabilization of paper. Ljubljana, National and University Library, pp. 27-47.
Strlič, M, Thomas, J, Trafela, T, Csefalvayova, L, Kralj Cigic, I, Kolar, J & Cassar, M (2009). *Material Degradomics: On the Smell of Old Books*. Analytical Chemistry 81(20): 8617–8622.
Strofer-Hua, E (1990). *Experimental measurement: Interpreting extrapolation and prediction by accelerated aging*. Restaurator 11(4): 254-266.
Wilson, KW & Parks, EJ (1980). *Comparison of accelerated aging of book papers in 1937 with 36 years natural aging*. Restaurator 4: 1-55.
Wilson, WK, Harvey, JL, Mandel, J & Worksman, T (1955). *Accelerated aging of record papers compared with normal aging*. TAPPI Journal 38(9): 543-548.
Wilson, WK & Parks, EJ (1983). *Historical survey of research at the National Bureau of Standards on materials for archival records*. Restaurator 5: 191-241.
Zervos, S (2007a). *Accelerated ageing kinetics of pure cellulose paper after washing, alkalization and impregnation with methylcellulose*. Restaurator 28(1): 55-69.
Zervos, S (2007b). *Evaluating treatments of paper using statistically valid test methods. Part II: Experimental setup and protocol*. Restaurator 28(4): 256-288.
Zervos, S (2010). Natural and accelerated ageing of cellulose and paper: A literature review. In: Lejeune, A & Deprez, T (eds.) Cellulose: Structure and Properties, Derivatives and Industrial Uses. New York, Nova Publishing, pp. 155-203.
Zervos, S & Moropoulou, A (2005). *Cotton cellulose ageing in sealed vessels. Kinetic model of autocatalytic depolymerization*. Cellulose 12(5): 485-496.
Zervos, S & Moropoulou, A (2006). *Methodology and criteria for the evaluation of paper conservation interventions. Literature review*. Restaurator 27(4): 219-274.
Zou, X, Gurnagul, N & Uesaka, T (1993). *The role of lignin in the mechanical permanence of paper. Part I: effect of lignin content*. Journal of Pulp and Paper Science 19(6): j235-j239.
Zou, X, Gurnagul, N, Uesaka, T & Bouchard, J (1994). *Accelerated aging of papers of pure cellulose: mechanism of cellulose degradation and paper embrittlement*. Polymer Degradation and Stability 43: 393-402.
Zou, X, Uesaka, T & Gurnagul, N (1996a). *Prediction of paper permanence by accelerated aging I. Kinetic analysis of the aging process*. Cellulose 3: 243-267.
Zou, X, Uesaka, T & Gurnagul, N (1996b). *Prediction of paper permanence by accelerated aging II. Comparison of the predictions with natural aging results*. Cellulose 3: 269-279.