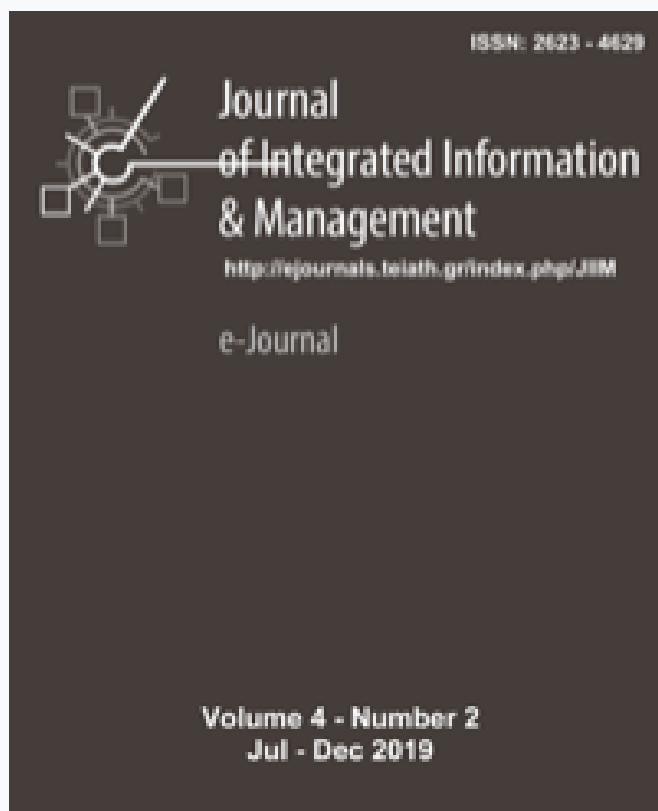


Journal of Integrated Information Management

Vol 4, No 2 (2019)

Jul-Dec 2019



University of West Attica

Pure cellulose paper ageing in sealed vessels. Autocatalytic depolymerization model revisited

Spiros Zervos, Konstantinos Choulis, Georgios Panagiaris

Copyright © 2019



This work is licensed under a [Creative Commons Attribution-NonCommercial 4.0](https://creativecommons.org/licenses/by-nc/4.0/).

To cite this article:

Zervos, S., Choulis, K., & Panagiaris, G. (2019). Pure cellulose paper ageing in sealed vessels. Autocatalytic depolymerization model revisited. *Journal of Integrated Information Management*, 4(2), 24–28. Retrieved from <https://ejournals.epublishing.ekt.gr/index.php/jiim/article/view/37874>

Pure cellulose paper ageing in sealed vessels. Autocatalytic depolymerization model revisited

Spiros Zervos¹, Konstantinos Choulis² and Georgios Panagiaris²

¹Department of Archival, Library & Information Studies, University of West Attica, Athens, Greece

²Department of Conservation of Antiquities & Works of Art, University of West Attica, Athens, Greece

szervos@uniwa.gr [ORCID: 0000-0003-1849-5999], kchoulis@uniwa.gr, gpanag@uniwa.gr

Article Info

Article history:

Received: August 2019

Received in revised form: November 2019

Accepted: December 2019

DOI: <https://doi.org/10.26265/jiim.v4i2.4419>

Abstract:

Purpose - In the framework of the EU funded INVENVORG project (Thales Research Funding Program – NRSF), the natural and artificial ageing of bone, wood, textiles, parchment and paper were investigated.

Design/methodology/approach - In this work, the results of accelerated ageing on pure cellulose paper in sealed vessels are reported. The properties studied include the degree of polymerization (which was converted to the percentage of broken glycosidic bonds), the tearing resistance, the pH and the L* and b* coordinates of the CIEL*a*b* color system. Ageing was performed in sealed vessels at 90°C και 76% RH for periods of 20, 40, 60, 80, 100, 120 and 140 days.

Findings - The results indicated an overall deterioration of all paper properties, which accelerates with time because of the production of volatile acidic species (autocatalysis). The evolution of paper properties through time was modeled efficiently by use of the equations proposed by Zervos and Moropoulou (2005) for the autocatalytic acid hydrolysis of pure cellulose paper, which were shown that also apply for following the changes of tearing resistance. The applicability of the model equations was also verified for other paper properties, such as the percentage of broken bonds (δ%) and the L* and b* coordinates of the CIEL*a*b* color system.

Index Terms - Cellulose ageing model; autocatalysis; tearing resistance; pH; optical properties; sealed vessels

I. INTRODUCTION

Various equations have been proposed to describe the evolution of paper and cellulose properties during accelerated ageing. The Ekenstam [1] equation (eq. 1) is the oldest, and its applicability and acceptance are almost universal. It can be derived either by assuming zero order kinetics or as an approximation of first order kinetics, and it applies to heterogeneous conditions, to acid hydrolysis in solutions and to thermal, photochemical and enzymatic degradation of cellulose, at the early stage of the reaction [2-16].

$$\frac{1}{DP_t} - \frac{1}{DP_0} = kt \quad (1)$$

where DP_t and DP_0 are the Degree of Polymerization values at times t and 0 , t the time and k the rate constant.

Variations of eq. 1, but also other equations derived by other approaches, have also been introduced by Calvini, Ding and Wang and others [17, 18, 19, 20, 21, 22, 23, 24, 16, 25, 26, 27, 28], taking into consideration autocatalysis and the slowing of the reaction because of the inaccessibility of the crystalline regions of cellulose.

In a previous paper [21], a kinetic model which applied to the autocatalytic depolymerization of cellulose in sealed vessels was presented. The model introduced a generalized equation (eq. 2) that predicted the evolution of several properties of pure cellulosic paper during accelerated ageing at 80°C and 75% RH, namely the percentage of the broken glycosidic bonds (δ%), the folding endurance, tensile strength, tensile energy absorption, stretch at break and the L* and b* coordinates of the CIEL*a*b* color system.

$$P = P_0 \pm C \cdot (2^{k \cdot t} - 1) \quad (2)$$

where P_0 and P are the values of the property P at time 0 and t , and C and k constants.

Equation 2, like the Ekenstam equation, holds for the early stage of degradation, until δ% reaches 0.6–0.7% with a corresponding DP of around 250, which is in the range of reported LODP (Leveling of Degree of Polymerization) values [2, 5, 7, 16]. The theoretical and mathematical evolution of the model equation is presented elsewhere [21].

In the present paper, another paper strength property, tearing resistance, was also studied concerning its conformance to the model, and the predictive value of the model equations was reconfirmed for δ%, and the L* and b* coordinates of the CIEL*a*b* color system for different conditions of ageing in sealed vessels (90°C and 75% RH).

The framework of this study was the EU funded INVENVORG project (Thales Research Funding Program – NRSF), which investigated the natural and artificial ageing of bone, wood, textiles, parchment and paper [29].

II. RELATED WORK

Whatman no 2 filter paper was used for the production of test strips, which has been used to model pure cellulose, since it consists of pure cotton cellulose with no additives, fillers or sizing¹. Their size (7.6 X 6.5cm) was determined by the requirements of the determination of the tearing resistance.

Thirty test strips were sealed in each of seven 3-liter glass jars equipped with a sealing spring and a silicon rubber ring, containing 150 ml of saturated solution of NaCl for the adjustment of the RH at 76% ±1% [30]. The jars were placed in an oven at 90 ±1 °C, in which they remained for 20, 40, 60, 80, 100, 120 and 140 days. The test strips were suspended with linen thread from the lid of the jar.

For the determination of the Tearing Resistance (TR), an Elmendorf instrument (Lorentzen and Wettre) was used. At least 10 measurements for each withdrawal time were performed. The samples were preconditioned and conditioned before the TR determination according to TAPPI T 402 om-88 [31] standard (23°C and 25% RH for 24 hours and 23±1°C and 50±2% RH respectively).

The color coordinates L* and b* of the CIEL*a*b* color system were determined by a Dr. Lange spectrophotometer LMG 183 colorimeter. Five measurements were taken for every test strip at random places and the mean was calculated.

The surface pH of paper was determined by use of a flat contact electrode according to TAPPI T 529 om-04 [32]. Three measurements were taken at random spots of three paper strips and averaged.

The mean Degree of Polymerization (DP) was determined by viscometry, according to the ASTM D 1795-96 [33] standard. An Ubbelohde viscometer was kept in a thermostatic bath at 25±0.1 °C, with a suitable capillary so that the efflux time was between 80-300 sec. Cellulose was dissolved in 0.5 M cupriethylenediamine hydroxide solution, manufactured by Merck. DP values were converted to δ% (percentage of

broken bonds during ageing time t) by use of equation 3 [3,21].

$$\delta\% = 100 \cdot \left(\frac{2}{DP_t} - \frac{2}{DP_0} \right) \quad (3)$$

where DP_t and DP₀ are the Degree of Polymerization values at times t and 0, and δ% the percentage of broken bonds at time t.

The experimental setup utilized in the ageing experiments has been tested for possible leakage before. The experiments reported in the 2005 paper have been based on the same setup, and weight measurements of the glass jars before and after ageing indicated that there was no weight loss. The repeatability of the experimental results was tested at that time with parallel and consecutive ageing experiments, and the results obtained shown so statistically significant differences

III. RESULTS AND DISCUSSION

The experimental (exp) and predicted (pred) values of the determined properties are presented in Table 1, together with the property evolution equation [21], the values of the regression coefficients, the coefficient estimations and their standard errors.

The kinetic model of cellulose depolymerization used here [21] applies to the autocatalytic acid hydrolysis of cellulose in sealed vessels and can predict the evolution of several important properties of pure cellulose paper under the experimental conditions of the ageing experiment (T=90°C, RH=76%). The production of acidic species during paper ageing has been demonstrated by several researchers [34, 35, 36, 37] and has been verified for the experimental setup used here [21]. The production of acidic species is also supported by the pH values of the aged samples (table 1).

Table 1. Experimental (exp) and predicted (pred) values of the determined properties. The pH value of 2.8 is an outlier, the very low pH value resulting from probable sample contamination.

Days of ageing	TR (mN)		DP	δ%		L*		b*		pH
	TR-exp	TR-pred	DP	δ%-exp	δ%-pred	L*-exp	L*-pred	b*-exp	b*-pred	
0	692	676	1493	0	0	97.64	96.75	1.92	2.42	5.7
20	667	662	1208	0.032	0.028	95.18	95.96	3.28	2.95	5.4
40	608	631	902	0.088	0.080	94.29	94.70	4.06	3.76	5.2
60	549	564	615	0.191	0.172	92.39	92.73	5.47	5.02	4.7
80	438	416	447	0.313	0.340	90.65	89.63	6.07	6.95	4.8
100	87	92	256	0.647	0.640	84.38	84.75	10.23	9.93	2.8
120	87		223	0.763		83.98		10.12		3.7
140	43		182	0.965		77.33		12.47		3.4
model equation	TR = TR ₀ - C (2 ^{kt} - 1)			δ% = C (2 ^{kt} - 1)		L* = L* ₀ - C (2 ^{kt} - 1)		b* = b* ₀ + C (2 ^{kt} - 1)		
R ²	0.994			0.996		0.973		0.964		
	Estimate	Std. Error		Estimate	Std. Error	Estimate	Std. Error	Estimate	Std. Error	
P ₀	676	16		-	-	96.75	0.77	2.42	0.57	
C	11.9	6.1		0.035	0.007	1.38	1.23	0.98	1.02	
k	0.025	0.020		0.043	0.003	0.033	0.011	0.031	0.013	

The model, according to the limitations set for its theoretical development, applies for values of δ% (percentage of broken bonds) below 0.6-0.7 (which

corresponds to DP values around 250). At that point starts the attack on cellulose crystallites, the rate of the hydrolysis reaction drops due to stereochemical hindrance and the

¹ <https://www.gelifesciences.com/en/gb/shop/whatman-laboratory-filtration/cellulose-filter-papers>

model ceases to apply [21]. As fig. 1 indicates, the limitation discussed above is verified by the experimental data, since the reaction starts to slow down at values of $\delta\%$ around 0.6% – 0.7%. According to the above, the applicability of the model was tested for the first 100 days of ageing corresponding to values of $\delta\% < 0.7$ (DP > 250). Figure 2 presents the plots of TR (Tearing resistance), $\delta\%$ (percentage of broken bonds), and L^* and b^* coordinates of the CIEL*a*b* color system against time of ageing. The high values of the regression coefficients presented in table 1 indicate that the fit of the experimental values to the model equation is quite satisfactory.

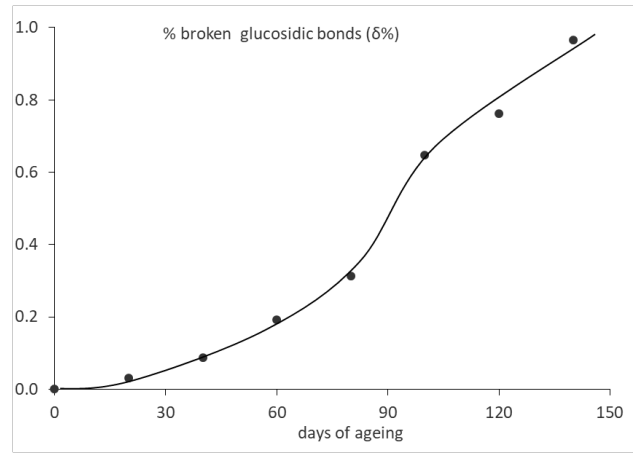


Figure 1. Plot of $\delta\%$ (percentage of the broken bonds) against time

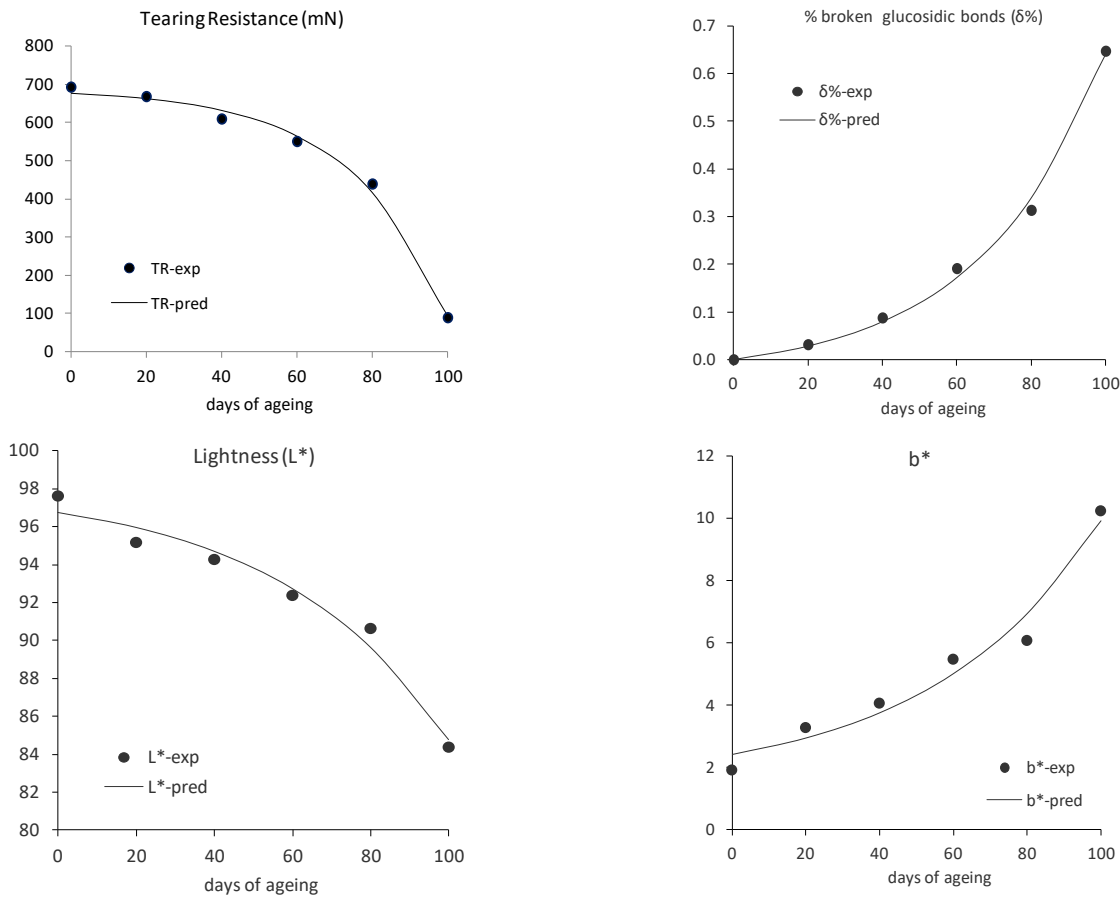


Figure 2. Plots of TR (Tearing resistance), $\delta\%$ (percentage of broken bonds), and L^* and b^* coordinates of the CIEL*a*b* color system against time of ageing. Experimental (exp, dots) and predicted (pred, lines) values.

In the previous report, it was shown theoretically that the pH of paper under those conditions of ageing (sealed vessels, autocatalysis) drops linearly with time ([21], eq. 14). The fitting of the experimental values of the previous study to a linear model gave inconclusive results but worked quite well with the pH values obtained by the present study, verifying what theory predicted (fig. 3). As mentioned above, the model works until $\delta\%$ approaches 0.6 - 0.7%. In many contexts, such as in paper conservation, this limitation is not

important, because at that point, the mechanical properties related to the usability of paper information substrates (mainly folding endurance) drop to such low values that the paper is not usable anymore [38].

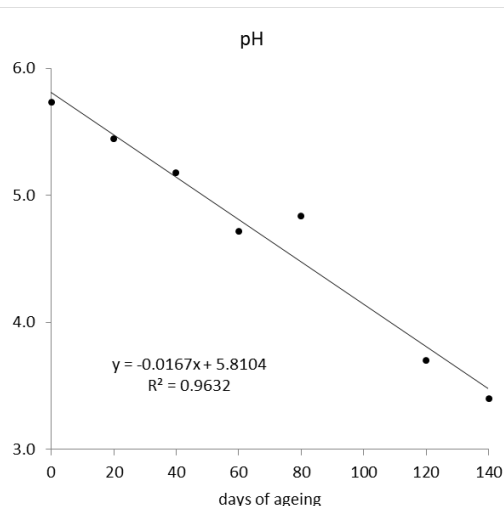


Figure 3. Surface pH of paper against time. The fit is satisfactory, as indicated by the high value of R^2 . The pH value of 2.8 is an outlier (see table 1) and was not taken into account.

IV. CONCLUSIONS

Accelerated ageing in sealed vessels results in an overall deterioration of important paper properties, which accelerates with time because of the production of volatile acidic species (autocatalysis). The evolution of pure cellulose paper properties can be modeled efficiently by use of the equations presented above. In this work, it was shown that the model of autocatalytic acid hydrolysis suggested by [21] can be effectively applied for following the changes of tearing resistance. The applicability of the model was also verified for other paper properties, such as the percentage of broken bonds ($\delta\%$) and the L^* and b^* coordinates of the CIEL*a*b* color system.

V. 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.

VI. REFERENCES

[1] Ekenstam, A (1936). The behaviour of cellulose in mineral acid solutions. Kinetic study of the decomposition of cellulose in acid solution (Über das Verhalten der Cellulose in Mineralsäure-Lösungen, II. Mitteil.: Kinetisches Studium des Abbaus der Cellulose in Säure-Lösungen). Berichte der Deutschen Chemischen Gesellschaft 69: 553-559.

[2] Krassig, H & Kitchen, W (1961). Factors influencing tensile properties of cellulose fibers. Journal of Polymer Science 51: 123-172.

[3] Michie, RIC, Sharples, A & Walter, AA (1961). The nature of acid-sensitive linkages in cellulose. Journal of Polymer Science 51: 131-140.

[4] Fung, DPC (1969). Kinetics and mechanism of the thermal degradation of cellulose. TAPPI Journal 52(2): 319-321.

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

[6] Marx-Figini, M & Coun-Matus, M (1981). On the kinetics of hydrolytic degradation of native cellulose. Die Makromolekulare Chemie 182(12): 3603-3616.

[7] 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.

[8] 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.

[9] 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.

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

[11] 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.

[12] Hill, DJT, Le, TT, Darveniza, M & Saha, T (1995). A study of degradation of cellulosic insulation materials in a power transformer, part 1. Molecular weight study of cellulose insulation paper. Polymer Degradation and Stability 48: 79-87.

[13] Zou, X, Uesaka, T & Gurnagul, N (1996). Prediction of paper permanence by accelerated aging I. Kinetic analysis of the aging process. Cellulose 3: 243-267.

[14] Kolar, J, Strlič, M, Malešič, J, Lemaire, J & Fromageot, D (2005). Photooxidative degradation. In: Strlič, M & Kolar, J (eds.) Ageing and stabilization of paper. Ljubljana, National and University Library, pp. 149-162.

[15] Gilbert, R, Jalbert, J, Tétrault, P, Morin, B & Denos, Y (2009). Kinetics of the production of chain-end groups and methanol from the depolymerization of cellulose during the ageing of paper/oil systems. Part 1: Standard wood kraft insulation. Cellulose 16(2): 327-338.

[16] 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.

[17] Emsley, AM, Heywood, RJ, Ali, M & Eley, CM (1997). On the Kinetics of Degradation of Cellulose. Cellulose 4: 1-5.

[18] Heywood, RJ, Stevens, GC, Ferguson, C & Emsley, AM (1999). Life assessment of cable paper using slow thermal ramp methods. Thermochemica Acta 332: 189-195.

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

[20] Ding, H-Z & Wang, ZD (2005). Modelling the ageing of cellulose insulation in power transformers. 3rd IEE international conference on reliability of transmission and distribution networks (RTDN 2005), London, UK, IEE Conference Publication, 508: 315-319.

- [21] Zervos, S & Moropoulou, A (2005). Cotton cellulose ageing in sealed vessels. Kinetic model of autocatalytic depolymerization. *Cellulose* 12(5): 485-496.
- [22] Calvini, P & Gorassini, A (2006). On the rate of paper degradation: lessons from the past. *Restaurator* 27: 275-290.
- [23] Calvini, P, Gorassini, A & Merlani, L (2007). Autocatalytic degradation of cellulose paper in sealed vessels. *Restaurator* 28(1): 47-54.
- [24] 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.
- [25] Ding, H-Z & Wang, ZD (2008a). Author response to the comments by P. Calvini regarding the article "On the degradation evolution equations of cellulose" by H.-Z. Ding and Z. D. Wang. *Cellulose* 15(2): 229-237.
- [26] Ding, H-Z & Wang, ZD (2008b). On the degradation evolution equations of cellulose. *Cellulose* 15(2): 205-224.
- [27] Calvini, P (2012). The role of the Ekenstam equation on the kinetics of cellulose hydrolytic degradation. *Cellulose* 19(2): 313-318.
- [28] Calvini, P (2014). On the meaning of the Emsley, Ding & Wang and Calvini equations applied to the degradation of cellulose. *Cellulose* 21(3): 1127-1134.
- [29] Zervos, S, Choulis, K & Panagiariis, G (2014). Experimental design for the investigation of the environmental factors effects on organic materials (Project INVENVORG). The case of paper. *Procedia - Social and Behavioral Sciences* 147: 39-46.
- [30] 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.
- [31] TAPPI T 402 om-88 (1988). Standard conditioning and testing atmospheres for paper, board, pulp handsheets and related products.
- [32] TAPPI T 529 om-04 (2004). Surface pH measurement of paper
- [33] ASTM D 1795-96 (R2001). Standard test method for intrinsic viscosity of cellulose.
- [34] 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.
- [35] Shahani, CJ & Harrison, G (2002). Spontaneous formation of acids in the natural aging of paper. In: Daniels, V, Donithorne, A & Smith, P (eds.) *Works of Art on paper, books, documents and photographs. Techniques and conservation*. Congress of the International institute for Conservation, Baltimore, MD. *Int. Inst. For Conservation*: 189-192.
- [36] 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.
- [37] Dupont, A-L, Egasse, C, Morin, A & Vasseur, F (2007). Comprehensive characterisation of cellulose- and lignocellulosedegradation products in aged papers: Capillary zone electrophoresis of low-molar mass organic acids, carbohydrates, and aromatic lignin derivatives. *Carbohydrate Polymers* 68 1-16.
- [38] Zervos, S & Moropoulou, A (2006). Methodology and criteria for the evaluation of paper conservation interventions. Literature review. *Restaurator* 27(4): 219-274.

VII. AUTHORS



Prof. Spiros Zervos holds a Chemistry degree and has been trained in Paper Conservation at the Centro del bel Libro in Ascona, Switzerland. He started his professional career in 1989 working as an Archival Material Conservator at the Corfu State Archives up until April 2009, when he was elected Assistant Professor in the

Department of Archival, Library and Information Studies. He teaches Conservation and Preservation of Archival and Library Materials and related topics. He obtained his PhD in material science in 2004 from the Chemical Engineering Department of the National Technical University of Athens. His research interests include paper and cellulose ageing, and conservation and preservation of paper and archival materials. Dr. Zervos is the first author and co - author of several publications - <http://users.uniwa.gr/szervos/>



Konstantinos Choulis studied painting and mosaic techniques at the School of Fine Arts in Athens, BA (1977-1983). With a scholarship obtained by the Hellenic Scholarship Foundation (I.K.Y.) he specialized in Paper Conservation and Restoration at the *Istituto Centrale per la patologia del libro* in Rome and in Greek Palaeography at the *Scuola di Paleografia,*

Diplomatica e Archivistica, Vatican City, MA (1984 -1985). He worked as Researcher in the Vatican Library on the Greek Byzantine bookbindings, supported by the Italian Institute of Culture in Athens (1986 - 1988). He obtained the PhD in the History of the Book, University of London, School of Advanced Study (2013). Since 1994 he has been teaching Book and Paper Conservation at the Department of Conservation of Antiquities and Works of Art of the former Technological Institute of Athens, now University of West Attica. He worked as Fellow Researcher at the *Istituto Centrale per la Patologia del Libro* in the project "Census of Medieval Bookbindings in Italian Libraries" (Rome, 1988-1992), as Senior Lecturer in the History of Early Bookbinding Techniques at the *Scuola Europea di formazione specialistica per conservatori - restauratori di Beni Librari*, Spoleto (Italy, 1992-2003), as Visiting consultant in the Grabar Institute (Moscow, 2008-2009) for the restoration of two Greek bookbindings (Synodal Gr. 407 and Khudov Psalter) and as visiting Professor in the summer courses (1 month) organized by the International Institute for Restoration and Preservation Studies (IIRPS) in San Gemini (Italy, 2011-2017). He is the author and co-author of numerous articles and monographies in the field of the conservation of manuscripts, bookbindings and works of art on paper.



George Panagiariis is Biologist, Doctor of Biological Sciences and licensed by the Greek Ministry of Culture as Conservator of Organic Materials. He is Professor at the Department of Conservation of Antiquities and Works of Art, University of West Attica, and Head of the same Department. He is a member of the ICOM

Conservation Committee with active participation in working groups dealing with collections of Natural History and Ethics Issues. His scientific / research activity focuses on issues of Conservation of Organic Materials with emphasis on human remains and collections of Natural History, issues of Biodeterioration in museum collections and on their ethical management. He has authored or coauthored over 150 publications. He has participated as main researcher or Coordinator in more than 40 Greek and International programs.