

# Accelerated Ageing Kinetics of Pure Cellulose Paper after Washing, Alkalization and Impregnation with Methylcellulose

**Spiros Zervos, Chemist & Paper Conservator**

Conservation Laboratory

General State Archives of Corfu

G.A.K. Archeia Nomou Kerkiras – Palaio Ffourio

GR 49100 Kerkira - Greece

tel: +302661038193

fax: +302661034784

e-mail: [szervos@otenet.gr](mailto:szervos@otenet.gr)

This is an edited version of the originally submitted manuscript (prereferred) of the article: “Accelerated Ageing Kinetics of Pure Cellulose Paper after Washing, Alkalization and Impregnation with Methylcellulose”, published in Restaurator, Volume 28, Issue 1, Pages 55–69, ISSN (Print) 0034-5806, DOI: 10.1515/REST.2007.55, 21/March/2007

The original publication is available at:

<http://www.reference-global.com/doi/abs/10.1515/REST.2007.55>

## Introduction

The studying of the accelerated ageing kinetics of cellulose has led to a general linear model that describes the change in some of its most important properties. The quantity  $\frac{1}{DP_t} - \frac{1}{DP_0}$ , which is proportional to the percentage  $\delta\%$  of the glycosidic bonds that break in time  $t^1$ , has been found to depend linearly on the time of ageing  $t^{2-11}$ :

$$\% \text{ broken bonds} = \delta\% = 100 \cdot \left( \frac{1}{DP_t} - \frac{1}{DP_0} \right) = k_1 t \quad (1)$$

where:  $DP_t$  and  $DP_0$  the number average degree of polymerization of cellulose at times  $t$  and  $0$  respectively and  $k_1$  constant. Equation 1 is valid for the initial stage of cellulose depolymerization, until  $\delta\%$  approaches the value of  $1\%$ <sup>5</sup>.

The change in folding endurance of paper has also been found to depend linearly on the time of ageing<sup>12-18, 6</sup>:

$$FE = FE_0 - k_2 t \quad (2)$$

where:  $FE$  and  $FE_0$  the folding endurance of paper at times  $t$  and  $0$  respectively and  $k_2$  constant. These kinetic laws apply to ageing in dry or humid circulating ovens and have been used extensively for following the ageing of cellulose and for paper permanence predictions<sup>19</sup>.

It has been proposed that ageing in sealed vessels simulates better the natural ageing of cellulose than ageing in circulating ovens and this setup has been incorporated in a new standard for paper ageing<sup>20-22</sup>. Shahani<sup>20</sup>, on the basis of folding endurance results which indicated an acceleration of the ageing rate, speculated that the process of ageing in sealed enclosures is autocatalytic. The alleged volatile acidic products of paper ageing were supposed to accumulate in the closed reaction space and brought about acceleration of the ageing, as their concentration increased. However, other researchers that used similar experimental setups (that is, not allowing for the volatile reaction products to escape) do not report acceleration of the reaction rate and their data conform well to the linear model<sup>10</sup> (eq. 1). Recently, Zervos & Moropoulou<sup>1</sup> provided evidence that the process of ageing of pure cellulose paper in sealed vessels is indeed autocatalytic and proposed a non-linear kinetic model based on autocatalysis that accounts for their experimental results. In this paper, we investigate the application of this non-linear model to the ageing of the same pure cellulose paper (Whatman no 2 filter paper), which has undergone washing, alkalization and impregnation with methylcellulose. These three treatments are standard conservation treatments that are very commonly used in conservation workshops. The implications of the proposed model are discussed, as far as the conservation and the preservation of library and archival material are concerned.

## Model presentation

The theoretical considerations that led to the creation of the model and the mathematical derivation of its equations are presented elsewhere<sup>1</sup>. Here, we shall introduce the mathematical expressions of the model and discuss the field of its application.

The primary equation of the model concerns the change of the percentage  $\delta\%$  of the glycosidic bonds that break in time of ageing  $t$ :

$$\delta \% = a (2^{k t} - 1) \quad (3)$$

where  $a$  and  $k$  are constants

From primary equation 3, the general equation 4 was derived which describes the change of a property  $P$  of the pure cellulose paper:

$$P = P_0 \pm C (2^{k' t} \pm 1) \quad (4)$$

where  $P$  and  $P_0$  the values of the property  $P$  in times  $t$  and  $0$  respectively and  $k'$  and  $C$  constants.

The properties of pure untreated cellulose paper (Whatman No 2) that were tested and found to conform to equation 4 are: folding endurance (FE), tensile strength (TS), stretch at break (SAB) and tensile energy absorption (TEA) from the mechanical properties and the  $L^*$  (lightness) and  $b^*$  (indicating yellowness) coordinates of the CIEL\*a\*b\* colour system from the optical properties.

The model has been found to work well for long ageing times of pure cellulose paper of around neutral pH and for values of  $\delta\%$  less than 0.7%. Such a limitation applies to the linear model as well<sup>5, 11</sup> and is practically insignificant, because at the time that  $\delta\%$  approaches this value, the usability of paper is completely lost, since folding endurance has dropped to zero. An integral role in the formulation of the model plays the fact that the volatile products of cellulose ageing are acidic. If these acidic products are removed, the linear model presented in the beginning of this paper prevails and the rate of paper degradation remains practically constant during the initial stage. Since, in the case of ageing in sealed vessels, the autocatalysis model predicts an acceleration of the reaction rate, the overall degradation is much faster and brings about an abrupt breakdown of paper.

## Experimental

The samples consisted of Whatman No 2 filter paper, which has been widely used to model pure cellulose, since it consists of pure cotton cellulose with no additives, fillers or sizing<sup>23</sup>. The washing of the samples with deionized water (samples H) and the treatment with semisaturated calcium hydroxide solution (“deacidification”, samples C) and 1% methylcellulose solutions (samples M) are presented elsewhere<sup>24</sup>.

Two series of experiments were performed. The first (designated Whatman X) included reference, washed, “deacidified” and methylcellulose impregnated samples. The second (designated Whatman U) included only reference and “deacidified” samples and was performed in order to verify and refine the results of the first series. Both experiments gave almost identical results. The first experiment served also for the rough estimation of the most suitable ageing periods. The ageing times for the first experiment were 40, 80, 120, 160 and 240 days and for the second experiment 30, 60, 90, 120 and 150 days, and the temperature was 80°C for both experiments. The ageing procedure was different for the two series. Samples “Whatman X” were aged in sealed 30 liters stainless steel vessels. The desired relative humidity was maintained around 75% by placing 4 Pyrex glasses containing 100 ml of saturated NaCl solutions inside the vessels.

The determination of the mechanical properties was done according to the appropriate ISO standard (ISO 1924-2<sup>25</sup> and 5626<sup>26</sup>). The samples were first preconditioned at 23°C and 25% RH for 24 hours and then conditioned at 23°C and 50% RH for another 24 hours (TAPPI T 402<sup>27</sup>). At least 10 determinations for every mechanical property were performed. The optical properties of the samples ( $L^*$  and  $b^*$  coordinates of CIEL\*a\*b\* color system) were determined by a spectrophotometer manufactured by Dr. Lange, model “spectrocolor LMG 183”.

$\delta\%$  was estimated from equation 1, by determining the viscosity-average degree of polymerization of cellulose according to ASTM 1795-96 standard<sup>28</sup> (mean of at least two determinations). The viscosity-average degree of polymerization ( $DP_v$ ) is approximately equal to the weight average degree of polymerization<sup>11</sup> ( $DP_w$ ). For natural samples of cellulose,  $DP_w$  is approximately twice the number average degree of polymerization ( $DP_w \approx 2 DP_n$ )<sup>29, 30</sup>. Specifics on the properties determination and the ageing procedure for “Whatman U” samples are described in previous papers<sup>24, 1</sup>.

## Results - Model Application

The results of the DP measurements were used for the calculation of  $\delta\%$ . The resulting figures of  $\delta\%$  were fit in the model equation 3 (non linear regression) by use of the statistical package SPSS v. 8 for Windows. The same statistical program was used to fit the results of the mechanical and the optical properties in equation 4. The results of the non linear regression for  $\delta\%$  and selected mechanical and optical properties are presented in the following graphs and tables.

For the sample series Whatman X, we present the values of the untreated (R), washed (H), “deacidified” (C) and methylcellulose (M) treated samples. The graphs extend up to 160 days except for X C series, which extends up to 240 days. This happens because around 160 days for the X R, X H and X M series and 240 for the X C series, all usability of paper is lost and  $\delta\%$  has reached the value of 0.7%, which is the upper limit of the applicability of the model. For the sample series U, we only present the results of the “deacidified” (C) samples. The results of the untreated samples (U R) have been presented elsewhere<sup>1</sup>.

Property	R	H	C	M
$\delta\%$	0.999	0.998	0.990	0.980
FE	0.997	0.990	0.990	0.984
TS	0.989	0.990	0.991	0.987
SAB	0.983	0.990	0.986	0.997
TEA	0.947	0.995	0.989	0.961
L*	0.998	0.989	0.997	0.995
b*	1.000	0.997	0.998	0.999

Table 1: Regression coefficients ( $R^2$ ) of the fits of various properties, Whatman X

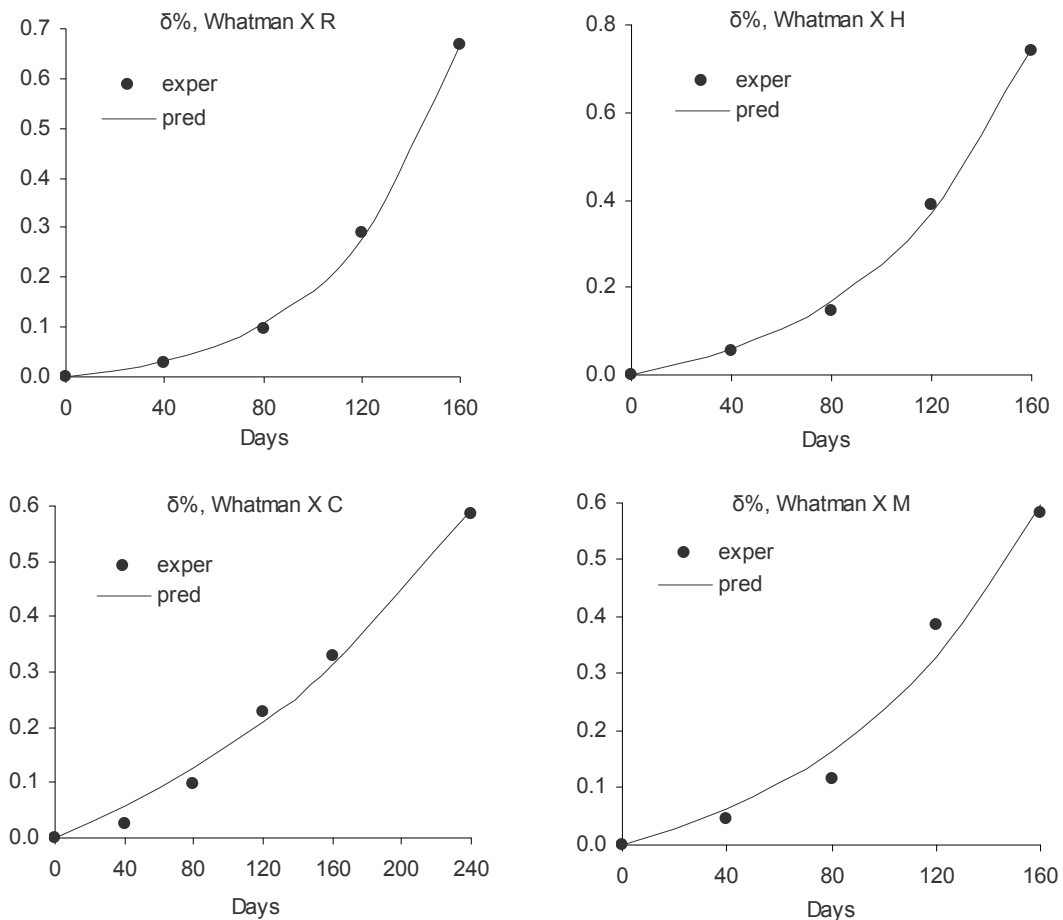


Figure 1:  $\delta\%$ , Whatman X. Experimental and predicted values

	R		H		C		M					
	DP	exper.	pred.	DP	exper.	pred.	DP	exper.	pred.	DP	exper.	pred.
0	1810	0.0000	0.0000	1633	0.0000	0.0000	1713	0.0000	0.0000	1639	0.0000	0.0000
40	1437	0.0286	0.0330	1142	0.0527	0.0584	1408	0.0253	0.0567	1196	0.0453	0.0627
80	974	0.0949	0.1082	739	0.1482	0.1671	938	0.0966	0.1259	839	0.1165	0.1645
120	499	0.2905	0.2793	392	0.3880	0.3692	578	0.2294	0.2103	395	0.3845	0.3296
160	257	0.6666	0.6689	232	0.7406	0.7452	447	0.3302	0.3132	284	0.5821	0.5973
240	185	0.9718		184	0.9672		285	0.5853	0.5918	187	0.9478	

Table 2: Experimental and predicted values of  $\delta\%$ , Whatman X

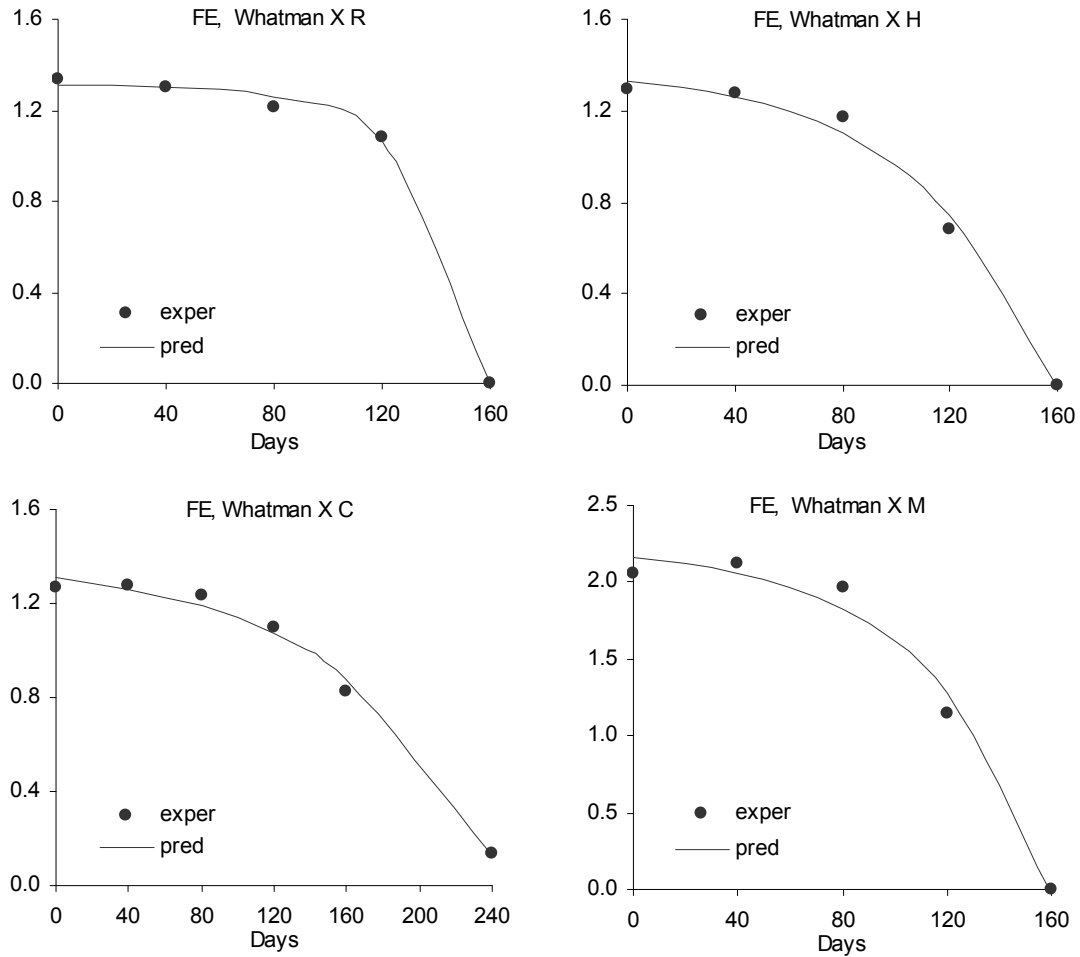


Figure 2: Folding Endurance, Whatman X. Experimental and predicted values

	R		H		C		M	
DAYS	exper.	pred.	exper.	pred.	exper.	pred.	exper.	pred.
0	1.34	1.31	1.29	1.33	1.27	1.31	2.05	2.16
40	1.30	1.30	1.28	1.26	1.27	1.26	2.12	2.06
80	1.21	1.26	1.17	1.10	1.23	1.19	1.97	1.82
120	1.08	1.06	0.68	0.74	1.10	1.07	1.15	1.27
160	0.00	0.00	0.00	-0.01	0.83	0.88	0.00	-0.03
240					0.14	0.13		

Table 3: Experimental and predicted values of Folding Endurance, Whatman X

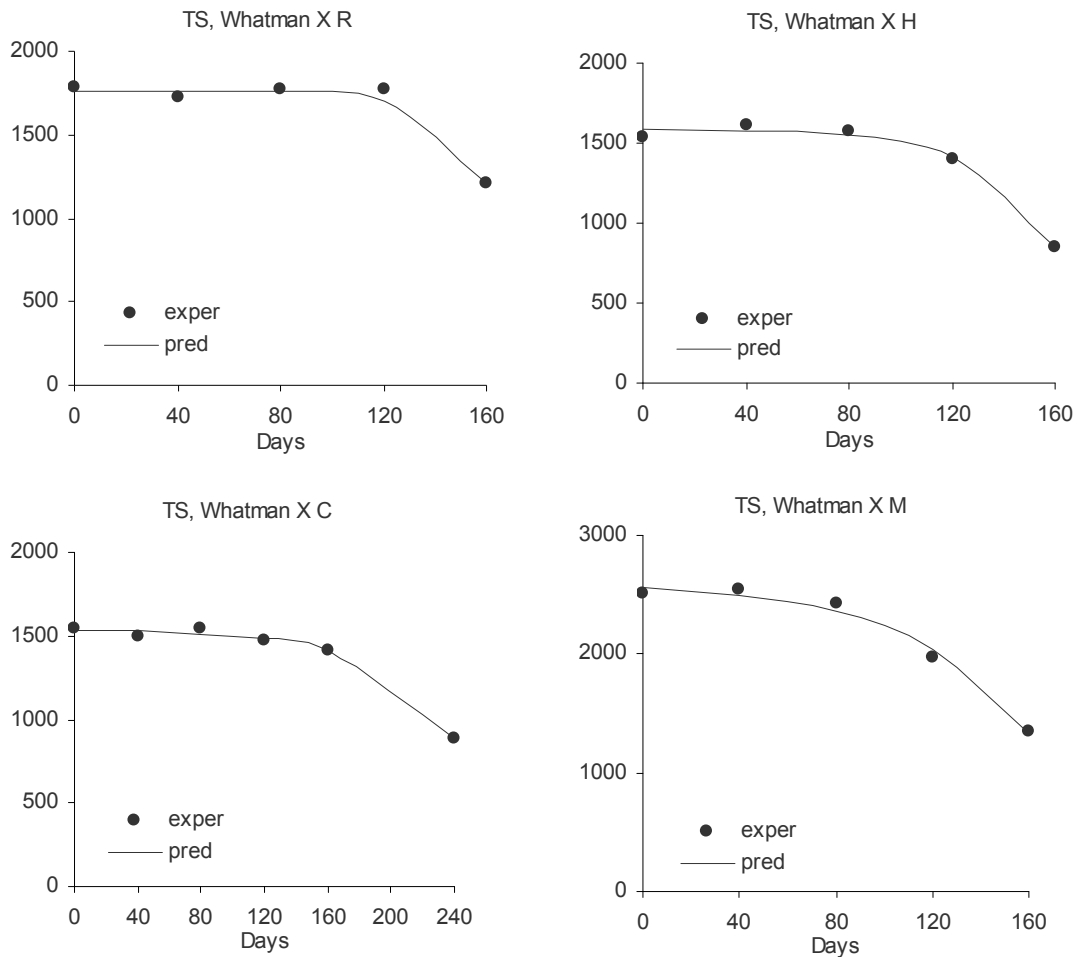


Figure 3: Tensile Strength, Whatman X. Experimental and predicted values

DAYS	R		H		C		M	
	exper.	pred.	exper.	pred.	exper.	pred.	exper.	pred.
0	1790	1765	1542	1587	1550	1535	2510	2565
40	1722	1765	1612	1579	1492	1529	2537	2501
80	1772	1765	1573	1546	1547	1515	2427	2359
120	1775	1763	1395	1411	1472	1484	1978	2041
160	1214	1215	854	852	1414	1413	1342	1329
240					892	892		

Table 4: Experimental and predicted values of Tensile Strength, Whatman X

	R		H		C		M	
	exper.	pred.	exper.	pred.	exper.	pred.	exper.	pred.
0	1.77	1.74	1.54	1.38	1.53	1.34	1.66	1.58
40	3.52	3.57	3.29	3.57	3.12	3.42	3.33	3.45
80	5.79	5.79	5.92	5.96	5.37	5.51	5.54	5.62
120	8.50	8.46	8.89	8.59	7.88	7.60	8.35	8.16
160	11.69	11.71	11.34	11.47	9.71	9.69	11.04	11.12
240					13.85	13.90		

Table 5: Experimental and predicted values of  $b^*$ , Whatman X

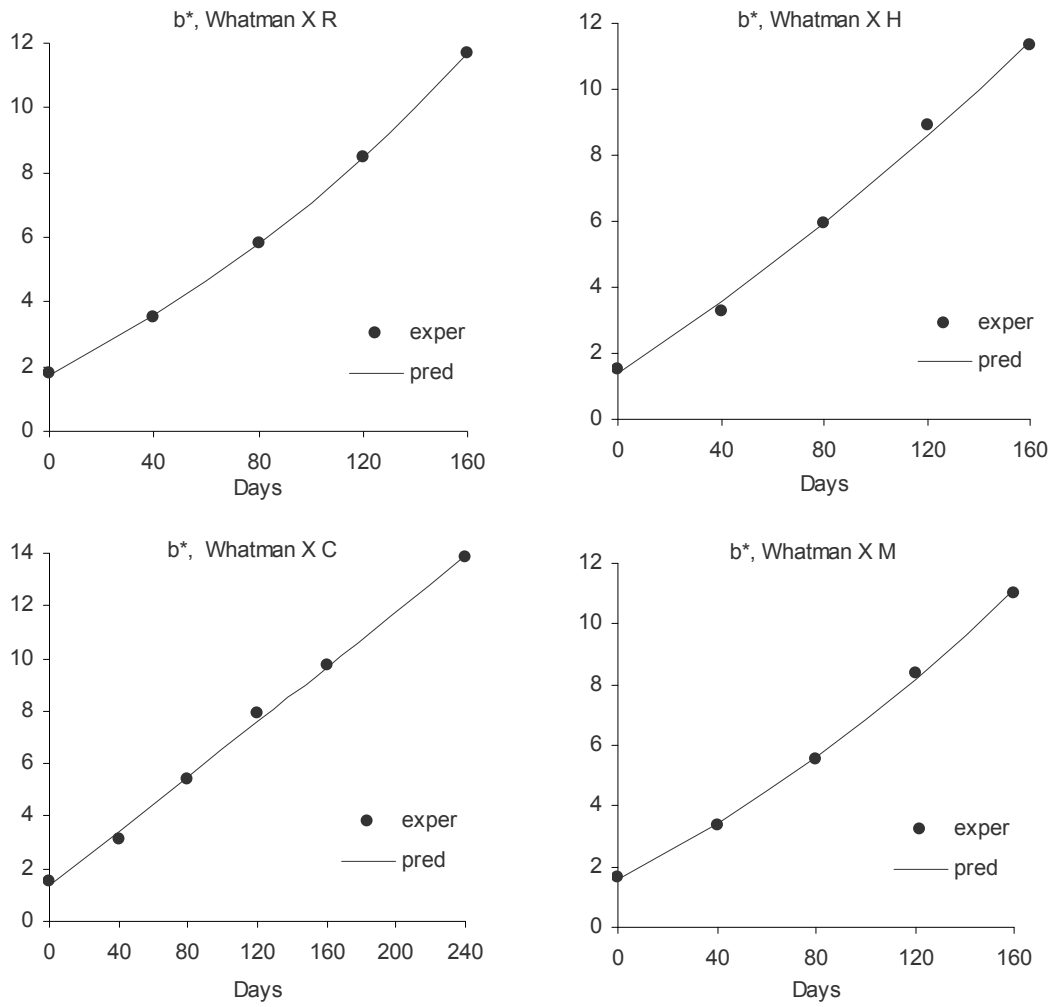


Figure 4:  $b^*$ , Whatman X. Experimental and predicted values

t	$\delta\%$		FE		TS		SAB		TEA		L*		$b^*$	
	exper.	pred.	exper.	pred.	exper.	pred.	exper.	pred.	exper.	pred.	exper.	pred.	exper.	pred.
0	0.0000	0.0000	1.30	1.29	1593	1625	3.65	3.61	47.4	46.2	97.68	97.79	1.74	1.80
30	0.0136	0.0174	1.28	1.28	1617	1623	3.38	3.50	41.7	44.7	96.54	96.35	2.88	2.80
60	0.0447	0.0475	1.24	1.26	1661	1616	3.40	3.30	43.8	41.9	94.81	94.76	3.89	3.90
90	0.0806	0.0995	1.23	1.21	1597	1592	2.99	2.97	37.0	36.8	92.80	93.00	5.17	5.11
120	0.2115	0.1891	1.06	1.07	1505	1519	2.37	2.42	27.2	27.8	91.11	91.05	6.32	6.45
150	0.3375	0.3438	0.73	0.73	1291	1288	1.48	1.47	11.6	11.5	88.91	88.90	7.98	7.92
$R^2$	0.990		0.995		0.962		0.992		0.984		0.998		0.999	

Table 6: Experimental and predicted values and regression coefficients ( $R^2$ ) of the fits of various properties, Whatman U C



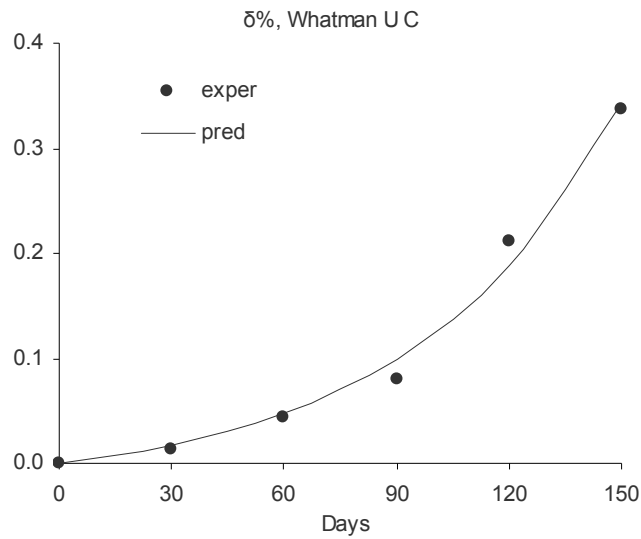


Figure 5:  $\delta\%$ , Whatman U C. Experimental and predicted values

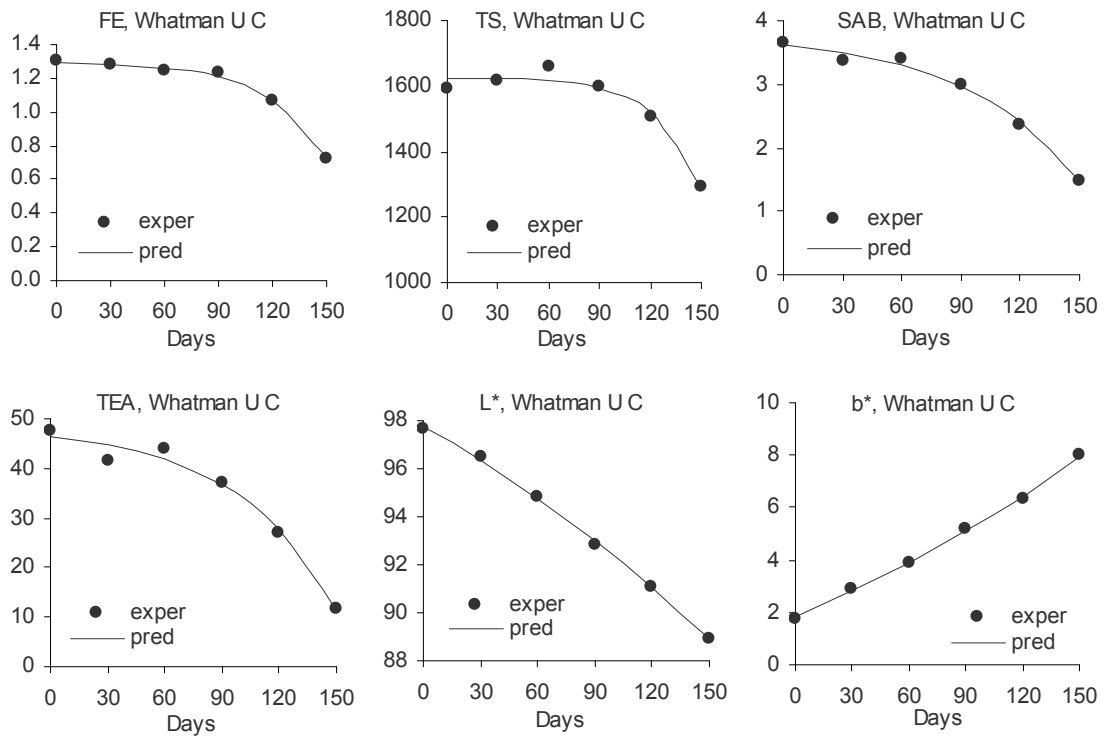


Figure 6: Various properties of Whatman U C. Experimental and predicted values

## Discussion

The results of the fits indicate that the model works equally well for the treated samples as it has been found to work for the untreated ones<sup>1</sup>. This is apparent from the high values of the regression coefficients of the fits (tables 1 and 6) and denotes that the chemistry of the degradation of the treated and the untreated samples is essentially the same.

We shall attempt to provide a qualitative interpretation of the degradation kinetics, explaining the issue of acceleration. It is well known that acid hydrolysis is the main degradation chemistry of cellulose. In the case of acid hydrolysis, a linear dependence of  $\delta\%$  upon time prevails. It has been proved that during accelerated ageing in sealed vessels, acidic volatile species are produced and accumulate inside the vessels<sup>1</sup>. The increase in the concentration of the acidic species leads to the acceleration of the reaction rate and that to the acceleration of the production of the acidic species and so on (autocatalysis). The overall result of this process leads to an exponential deviation of the linear scheme that should be expected if autocatalysis did not occur.

It has been proposed that ageing in sealed vessels simulates better the natural ageing of paper stored in libraries and archives than ageing in circulating ovens for a number of reasons<sup>19, 20</sup>. The main argument supporting this notion is that in real life paper ages together with large quantities of other paper in environments (either inside books, files, cabinets or other enclosed spaces) that do not allow for the replenishment of the air, permitting thus the accumulation of the products of paper degradation. Since paper degradation products are acidic, it seems plausible that their presence must affect the degradation process and that any method implemented for paper ageing acceleration should take that into account. On that basis, we believe that our results allow for a better prediction of the behaviour of real paper in real life than the linear model.

The limiting value of  $\delta\%$  ( $\sim 0.7\%$ ,  $DP_v$  around 250) that the model is valid arises from the initial theoretical assumptions necessary for the formulation of the model, but also from the experimental results. When  $\delta\%$  reaches that value, the exponential increase ceases and the reaction rate drops (fig. 7). Such a deceleration of the reaction rate has been observed by others and is attributed to the stereochemical hindrance. Around these values of DP (reported values range between 400 and 200<sup>31, 30, 5</sup>), hydrolysis starts to attack the crystalline regions, which are much more compact than the amorphous, and the reaction rate drops. It is remarkable that the DP of R, H and M samples of the Whatman X series, converge around the value of 185 at 240 days of ageing (table 2), indicating that the stereochemical hindrance works very similarly for all the non-deacidified samples.

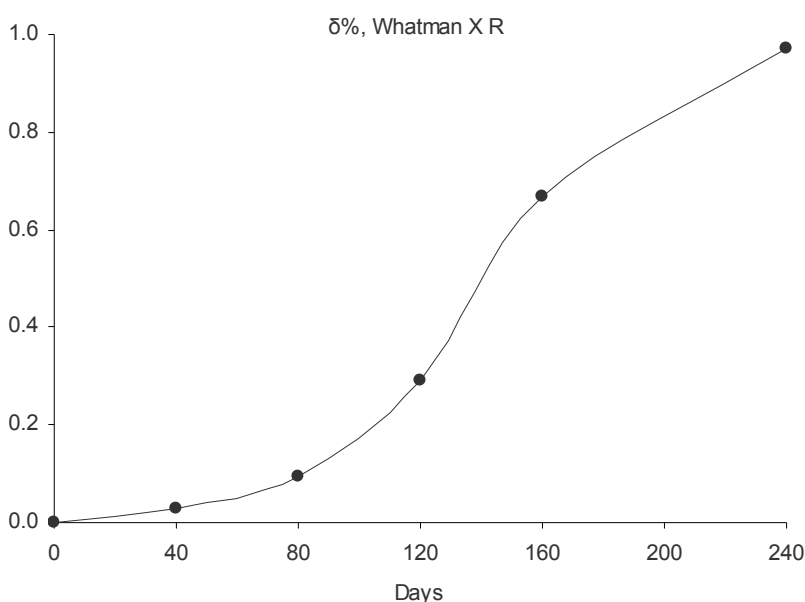


Figure 7:  $\delta\%$ , Whatman X R

We believe that we have presented enough evidence that prove the applicability of the model on the ageing of pure treated and untreated cellulose paper in sealed vessels. It seems plausible that the same model should apply on historical paper, especially paper with high content of cellulose, although such an assumption should be verified. On that basis, we shall leave aside the formalism of the model and try to decipher its consequences upon paper preservation and conservation.

A qualitative interpretation of the model equations indicates that at the end of a phase of acceleration of the degradation, folding endurance drops abruptly to zero. This is also evident from the graphs of folding endurance. The established linear model for paper ageing in circulating ovens predicts a constant rate of degradation, which must be similar to the initial rate of the proposed exponential model. Thus, it can be concluded that the exponential model predicts a much faster deterioration of paper and that the loss of paper usability is not gradual but happens abruptly (fig. 8). The above presented evidence support Shahani's opinion<sup>20</sup> that the time margin for implementing active measures for the preservation of our written heritage is less than it was thought of. The fact that paper stored in libraries and archives has survived for a long time does not guarantee its preservation for even longer times, because as it was demonstrated, its collapse will not happen gradually but abruptly.

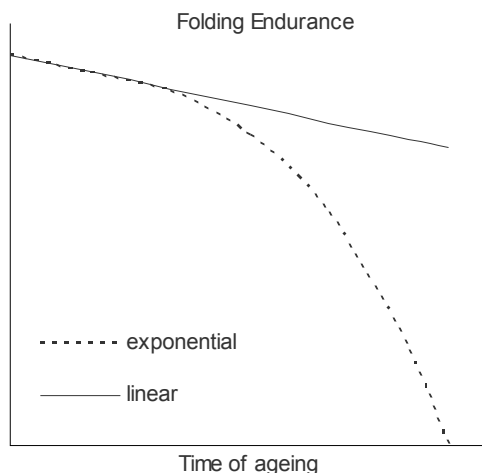


Figure 8: Schematic diagram of folding endurance indicating the difference between the established linear and the proposed exponential model

While the accumulation of the volatile paper degradation products is responsible for the acceleration of the reaction rate (sealed vessels), their removal from the reaction space leads to linear kinetics and lower rates of degradation (circulating ovens). This fact points to a preservation principle which is easily stated but not so easily implemented: "The ventilation of the repositories and the circulation of clean air reduces the concentration of the volatile paper degradation products, reducing at the same time the degradation rate of paper". The removal of volatile acidic species can also be accomplished by chemical means. The recycling of the air through chemical filters containing alkaline substances can be incorporated to an existing air-conditioning system. The use of alkaline substances for painting or coating the repositories could also serve as a temporary measure. The encapsulation of acidic paper should be avoided. Paper should be encapsulated only after deacidification or else alkaline paper should be enclosed together with the original<sup>20</sup>. The storage of paper in air tight boxes, chests or closets is not recommended and the shelving systems used in archives and libraries should provide for adequate ventilation.

It is widely accepted that “usage is an enemy to preservation”. This tenet is based on the fact that handling and studying books and archival material unavoidably inflicts damage on them, either mechanical because of mistreatment or chemical through the absorption of perspiration. Nevertheless, the simple act of removing a book from the shelf and browsing through it stirs the air around it and removes a part of the entrapped volatile acids. On that basis, proper usage could have positive results apart from the established negative ones.

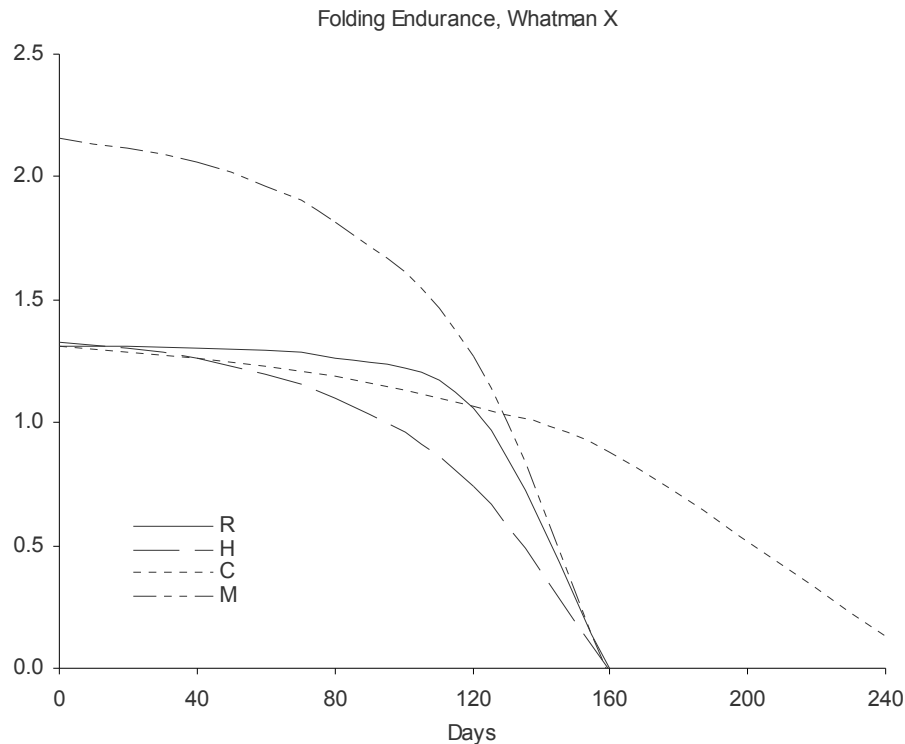


Figure 9: Folding Endurance, Whatman X (predicted curves)

In figure 9, the predicted curves of folding endurance of all four series of Whatman X samples are presented together. The graph indicates that:

- Washing with deionized water weakens slightly the ageing resistance of paper.
- Consolidation with methylcellulose strengthens paper significantly and has no negative effect on the rate of ageing. The ageing behaviour of the treated paper is better than the untreated for the whole course of ageing.
- Deacidification with semisaturated calcium hydroxide solution prolongs paper’s useful life (in this case, approximately by a factor of 0.5). The positive contribution of deacidification becomes apparent in the last part of the ageing curve, after around 120 days of ageing, when all the other samples start to collapse. The deceleration of the collapsing stage of paper ageing seems to be the main positive effect of the treatment.

## Conclusions

The high values of the regression coefficients of the fits indicate that the exponential model proposed is applicable to pure cellulose paper which has undergone the three most important conservation treatments, that is washing, deacidification and strengthening by immersion in methylcellulose. The properties that conform to the model are: percentage of broken glycosidic bonds ( $\delta\%$ ), folding endurance (FE), tensile strength (TS), stretch at break (SAB), tensile energy absorption (TEA) and the  $L^*$  (lightness) and  $b^*$  (indicating yellowness) coordinates of the CIEL\*a\*b\* colour system.

The experimental results and the model equations indicate that:

- Paper degradation in libraries and archives is faster than the linear model predicts
- The breakdown of paper occurs abruptly and the fact that paper has survived for long time does not guarantee its further survival
- The “enemy” in the form of detrimental air-borne pollution does not only come from the outside, but is also generated inside the repositories of libraries and archives
- The ventilation of the storage areas in libraries and archives and the circulation of clean air is a crucial preservation factor
- The proper usage of books and archival material could have a positive effect on their preservation because it facilitates the removal of the detrimental acidic products of paper degradation

## **Acknowledgements**

I wish to thank the dear colleagues, Dimitra Barba and Tina Togonalidou, for their contribution to the DP determination and the elaboration of the model equations respectively.

## **Abstract**

The applicability of an exponential model based on autocatalysis to the ageing kinetics of pure cellulose paper, which has undergone washing, alkalization and impregnation with methylcellulose is investigated. The properties that were found to conform to the model are: percentage of broken glycosidic bonds, folding endurance, tensile strength, stretch at break, tensile energy absorption and the L\* and b\* coordinates of the CIEL\*a\*b\* colour system. The implications of the model concerning paper preservation are discussed. It is concluded that paper degradation in libraries and archives is faster than the linear model predicts and that the ventilation of the storage areas and the circulation of clean air is a crucial preservation factor because it facilitates the removal of the detrimental acidic products of paper degradation.

## References

1. Zervos, S., & Moropoulou, A.: *Cotton cellulose ageing in sealed vessels. Kinetic model of autocatalytic depolymerization*. Cellulose 12 (5) (2005): 485-496.
2. Ekenstam, A.: *The behaviour of cellulose in mineral acid solutions. Kinetic study of the decomposition of cellulose in acid solution*. Ber. Deutschen Chem. Gesellschaft 69 (1936): 553.
3. Fung, D.P.C.: *Kinetics and mechanism of the thermal degradation of cellulose*. TAPPI Journal 52 (2) (1969): 319-321.
4. Shafizadeh, F., & Bradbury, A.G.W.: *Thermal degradation of cellulose in air and nitrogen at low temperatures*. Journal of Applied Polymer Science 23 (1979): 1431-1442.
5. Feller, R.L., Lee, S.B., & Bogaard, J.: *The kinetics of cellulose deterioration*. In: Needles H.L., Zeronian, S.H., eds. *Historic Textile and Paper Materials - Conservation and Characterization*. Advances in Chemistry Series, 212. Washington DC: American Chemical Society, 1986: 329-347.
6. Fellers, C., Iversen, T., Lindstrom, T., Nilsson, T., & Rigdahl, M.: *Ageing/Degradation of paper, a literature survey*. FoU-projektet for papperskonservering, Report No. 1 E, Stockholm 1989.
7. Emsley, A.M., & Stevens, G.C.: *Kinetics and mechanisms of the low-temperature degradation of cellulose*. Cellulose 1 (1994): 26-56.
8. Zou, X., Gurnagul, N., Uesaka, T., & Bouchard, J.: *Accelerated aging of papers of pure cellulose: Mechanism of cellulose degradation and paper embrittlement*. Polymer Degradation and Stability 43 (1994): 393-402.
9. Hill, D.J.T., Le, T.T., Darveniza, M., & Saha, T.: *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 (1995): 79-87.
10. Zou, X., Uesaka, T., & Gurnagul, N.: *Prediction of paper permanence by accelerated aging I. Kinetic analysis of the aging process*. Cellulose 3 (1996): 243-267.
11. Klemm, D., Philipp, B., Heinze, T., Heinze, U., & Wagenknecht, W.: *Comprehensive Cellulose Chemistry, Volume 1, Fundamentals and Analytical Methods*. Weinheim: Wiley – VCH, 1998.
12. Browning, B., & Wink, W.: *Studies on the permanence and durability of paper - I. Prediction of paper permanence*. TAPPI Journal 51 (4) (1968): 156-163.
13. Gray, G.: *An accelerated-aging study comparing kinetic rates vs. TAPPI standard 453*. TAPPI Journal 52 (2) (1969): 325-334.
14. Gray, G.G.: *Determination and significance of activation energy in permanence tests*. In: Williams, J.C., ed. *Preservation of paper and textiles of historic and artistic value*. Advances in Chemistry Series, 164. Washington DC: American Chemical Society, 1977: 286-313.
15. Walker, B.F.: *Morpholine deacidification of whole books*. In: Williams, J.C., ed. *Preservation of paper and textiles of historic and artistic value*. Advances in Chemistry Series, 164. Washington DC: American Chemical Society, 1977: 72-87.
16. Williams, J.C., Fowler, C.S., Lyon, M.S., & Merrill, T.L.: *Metallic catalysts in the oxidative degradation of paper*. In: Williams, J.C., ed. *Preservation of paper and textiles of historic and artistic value*. Advances in Chemistry Series, 164. Washington DC: American Chemical Society, 1977: 37-61.

17. Roberson, D.: *Permanence / durability and preservation. Research at the Barrow Laboratory*. In: Williams, J.C., ed. *Preservation of paper and textiles of historic and artistic value II*. *Advances in Chemistry Series*, 193. Washington DC: American Chemical Society, 1981: 45-55.
18. Tang, L.C.: *Washing and deacidifying paper in the same operation*. In: Williams, J.C., ed. *Preservation of paper and textiles of historic and artistic value II*. *Advances in Chemistry Series*, 193. Washington DC: American Chemical Society, 1981: 63-86.
19. Zervos, S. & Moropoulou, A.: *Methodology and criteria for the evaluation of paper conservation interventions. Literature review*. *Restaurator* (in press).
20. Shahani, C.: *Accelerated aging of paper: Can it really foretell the permanence of paper*. *Preservation Research and Testing Series* 9503 (1995). <http://lcweb.loc.gov/preserv/rt/age/>
21. Begin, P.L., & Kaminska, E.: *Thermal accelerated ageing test method development*. *Restaurator* 23 (2) (2002): 89-105.
22. ASTM D6819-02e2 (2002): *Standard test method for accelerated temperature aging of printing and writing paper by dry oven exposure apparatus*.
23. Whatman International L.t.d. Technical reference - Filter types, available at: [http://www.whatman.com/tech\\_support/archives/tech\\_archives\\_002.html](http://www.whatman.com/tech_support/archives/tech_archives_002.html)
24. Moropoulou, A., & Zervos, S.: *The immediate impact of aqueous treatments on the strength of paper*. *Restaurator* 24 (3) (2003): 160-177.
25. ISO 1924-2 (1992): *Paper and board – Determination of tensile properties – Part 2: Constant rate of elongation method*.
26. ISO 5626 (1993): *Paper – Determination of folding endurance*.
27. TAPPI T402 om-88 (1988): *Standard conditioning and testing atmospheres for paper, board, pulp handsheets and related products*.
28. ASTM D 1795 – 96 (1996, reapproved 2001): *Standard test method for intrinsic viscosity of cellulose*.
29. Michie, R.I.C., Sharples, A. & Walter A.A.: *The Nature of acid-sensitive linkages in cellulose*. *Journal of Polymer Science* 51 (1961): 131-140.
30. Shafizadeh, F., & Bradbury, A.G.W.: *Thermal degradation of cellulose in air and nitrogen at low temperatures*. *Journal of Applied Polymer Science* 23 (1979): 1431-1442.
31. Krassig, H., & Kitchen, W.: *Factors influencing tensile properties of cellulose fibers*. *Journal of Polymer Science* 51 (1) (1961): 23-172.