Methodology and Criteria for the Evaluation of Paper Conservation Interventions. Part 2: Experimental Study - Protocol Proposal

Spiros Zervos
Chemist & Paper Conservator
Conservation Laboratory
General State Archives of Corfu
G.A.K. Archeia Nomou Kerkiras – Palaio Frourio
49100 Corfu - Greece
tel: +302661038193
fax: +302661034784
e-mail: szervos@otenet.gr

This is an edited version of the originally submitted manuscript (prerefereed) of the article: "Methodology and Criteria for the Evaluation of Paper Conservation Interventions. Part 2: Experimental Study - Protocol Proposal", published in Restaurator under the title "Evaluating Treatments of Paper Using Statistically Valid Test Methods Part II: Experimental Setup and Protocol", Volume 28, Issue 4, Pages 256–288, ISSN (Print) 0034-5806, DOI: 10.1515/REST.2007.256, /December/2007
The original publication is available at:
http://www.reference-global.com/doi/abs/10.1515/REST.2007.256

INTRODUCTION

In the first part of this article, the results of a literature survey concerning the methodology used for the evaluation of paper conservation interventions have been presented[1]. The methodology generally consists of sample selection and preparation, experimental planning, ageing method, methods for the determination of paper properties and criteria of effectiveness. In this second part, the most important methods used for the determination of paper properties, which were produced by the survey and presented in the first part, are tested on various samples of paper treated with three standard conservation treatments and the results are statistically elaborated. On the basis of these results, the most sensitive and repeatable methods are chosen and a loose experimental protocol for the evaluation of paper conservation interventions is proposed.

In order to keep the project to a manageable size, it was decided not to test all the methods presented in the first part. The general rationale concerning the choice of the methods tested here has been presented in the first part of this article. The following criteria were also taken into consideration:

- Chemical, mechanical and optical properties should be examined
- The properties determined by the chosen methods must constitute fundamental representatives of the property class
- At least one of the mechanical properties should relate to the usability of paper
- Bibliographical data should indicate high sensitivity towards accelerated ageing and high repeatability and reproducibility
- Non-destructive and little-intervening methods are preferred
- The methods should preferably be simple, economic in terms of sample, time and resources and not requiring highly sophisticated equipment
- The interpretation of the results must be as straightforward as possible, preferably not requiring complex theoretical background
- A preferably fast and little intervening method for the characterization of paper would be desirable.

According to the above, the following sample properties were determined in this study:

- Folding Endurance (FE), ISO 5626[2].
- Tensile Properties: Tensile strength (TS), stretch at break (SAB) and tensile energy absorption (TEA), ISO 1924-2[3]). Can be simultaneously recorded with the same instrument and on the same samples.
- Cold extraction pH, (ISO 6588[4]).
- Degree of polymerization (DP). It was determined according to ASTM D 1795-96[5] from the intrinsic viscosity of cellulose solutions. From the DP values, δ%[6] (the percentage of the hydrolyzed glycosidic bonds) was calculated.
- Moisture content (M%). Necessary for the determination of the dry mass of paper. It is supposed to decrease with accelerated ageing.

The following methods were also used:

- Colorimetry. The L*, a* and b* coordinates of the CIEL*a*b* colour system and the Brightness (B), Yellowness index (Yi) and Whiteness index (Wi) were determined.
- Fourier Transform Infrared Spectroscopy (FTIR).
- Spot testing: Phloroglucinol test for the detection of lignin (TAPPI 401[7]) and Raspail test (TAPPI 408[8]) for the detection of rosin and the characterization of the pulp type (chemical or mechanical) and of the sizing system respectively.

The principles and the application of these methods for the study of paper properties and for the evaluation of paper conservation treatments have been presented in the first part of this article. From the mechanical properties, folding endurance and tensile properties were chosen for testing. The bibliographical data indicated that the other mechanical tests offer no more information about paper usability while they require considerable quantity of sample paper.

Chemical methods such as alkali solubility, copper number and kappa number, though valuable for routine testing in the paper industry were not tested because of their empirical nature.

Some complementary methods were also utilized, facilitating the understanding of structural changes of paper induced by conservation treatments and ageing on macroscopic and microscopic level:

- X-Ray Diffraction (XRD) for the determination of crystallinity changes. The crystallinity index[9] (CI) was determined by XRD.
- Fibre Optics Microscopy[10] (FOM) for the observation of the area of tensile failure.
- Water Vapour Adsorption. Water was used as a structural probe for the determination of microstructural changes.

When studying the feasibility of a conservation method, the objectives of the researchers vary; some study the immediate impact of the method under study, others the long-term results on the stability of paper towards accelerated ageing, while others both. For the study of the immediate impact, two categories of sample are needed (untreated, treated), and one comparison between the results of the two categories is sufficient. Likewise, for the study of the long term results, another two categories are necessary (untreated and aged, treated and aged) and again one comparison is involved. Since long term results are equally and very often more important than the immediate ones, a thorough research should study both. Accordingly, in an evaluation scheme of a conservation method, four categories of samples (untreated, treated, untreated and aged, and treated and aged) and two comparisons are necessary. Although this scheme may seem sufficient, a very important aspect of the effect of the treatment under study has been left out. This aspect concerns the effect of the treatment on the rate of ageing, or more precisely, the average rate of property change due to accelerated ageing. Including this aspect into the scheme, another comparison must be introduced, that of the rates of the property change of the treated and the untreated samples (Table 1).

Table 1: Comparisons between the four sample categories (*P*: Property, *R*: Reference sample, *T*: Treated sample, *o* and *a* stand for unaged and aged samples).

Immediate Impact	Long term effects:	Effect of treatment on the rate of ageing
Comparison of the property values of treated and untreated samples (P_{Ro} with P_{To})	Comparison of the property values of treated and untreated samples after accelerated ageing (P_{Ra} with P_{Ta})	Rate of ageing of reference sample $V_R = \frac{P_{Ro} - P_{Ra}}{t}$ Rate of ageing of treated sample $V_T = \frac{P_{To} - P_{Ta}}{t}$ Comparison of V_R with V_T

The statistical elaboration of the results constitutes another important aspect of the evaluation. The use of the student t-test or other relative statistical test (ANOVA: analysis of variance) is necessary for ascertaining that an alleged improvement or deterioration indicated by one of the possible comparisons presented above is real[11]. Student t-test is incorporated in all statistical programs (even in advanced spreadsheets like Microsoft Excel®) and by simply inserting the two groups of values that produce the two means, it determines whether the difference between these two means is statistically significant, that is, real, and not a result of an acceptable variance. The correlation coefficient is another useful statistical tool that indicates whether two variables are somehow related to each other. Finally, in this research, the determination of a variance estimator such as standard deviation or confidence interval facilitated the comparison of the repeatability of the different methods used here.

EXPERIMENTAL

The general concept of the evaluation is based on the determination of the short and long-term results of the intervention. The long-term results are studied on artificially aged samples. It also incorporates the comparison of the ageing rate of treated and untreated samples (see table 1).
In this study:

- The samples were subjected to the following conservation treatments:
  - Immersion in deionized water (Treatment symbol: H)
  - Immersion in semisaturated solution of calcium hydroxide, $Ca(OH)_2$ (Treatment symbol: C)
  - Immersion in 1% methylcellulose solution (Treatment symbol: M)

  Accordingly, four subseries of samples were produced: reference (R), washed (H), deacidified (C) and consolidated (M). Specifics on the treatments have been presented elsewhere[11]. Treatments H and M applied only to selected sample series. Instead of the standard consolidation treatment, a combined deacidification and consolidation was applied to the sample series Y, (treatment symbol: C+M). This treatment consisted of sample immersion in semisaturated calcium hydroxide solution containing 1% methylcellulose.
  The conservation treatments tested here were selected because they:
  - Represent the 3 general categories of paper conservation interventions: cleaning, chemical stabilization and consolidation (strengthening) by impregnation. Almost every conservation intervention (mending with Japanese paper excluded), can be classified in one of the above categories.
  - Are the most commonly used worldwide
  - Are easily reproducible
  - Have been extensively studied
  - Are easily applied, not requiring high technological infrastructure
  - Do not utilize toxic and dangerous reagents to human health
- The samples were artificially aged for suitable time intervals (table 3). Whatman samples X and U were aged for 5 time intervals, so that the kinetic study of ageing was feasible[6, 12]. The historical samples were aged for one time interval only, because historical paper was scarce.
- The properties of the samples in their original state, after ageing, after conservation, and after conservation and ageing were determined by the methods presented above. The results of the four sample categories were compared and conclusions concerning the success of the interventions were drawn (table 1, figure 1). Details concerning the practical aspect of the determination of the various paper properties have been presented in previous papers[6, 11].
- Statistical analysis, including student t-test and standard deviation, confidence interval and correlation coefficient determination was applied to the experimental results. The student t-test was used for the comparison of the average values of various paper properties. The correlation coefficient was calculated between any pair of paper properties, thus facilitating the determination of interdependent properties. The various methods tested here were compared on the grounds of their ability to detect minor changes (sensitivity), their repeatability, and their sample requirements. Thus, the feasibility of their application was evaluated and decided whether they would be included in the proposed evaluation methodology.
- The general criteria presented in the first part were encoded according to table 1 and applied to the experimental results for the evaluation of the three interventions tested here.
  The general scheme of the experimental setup is shown as a flow-chart in figure 1.

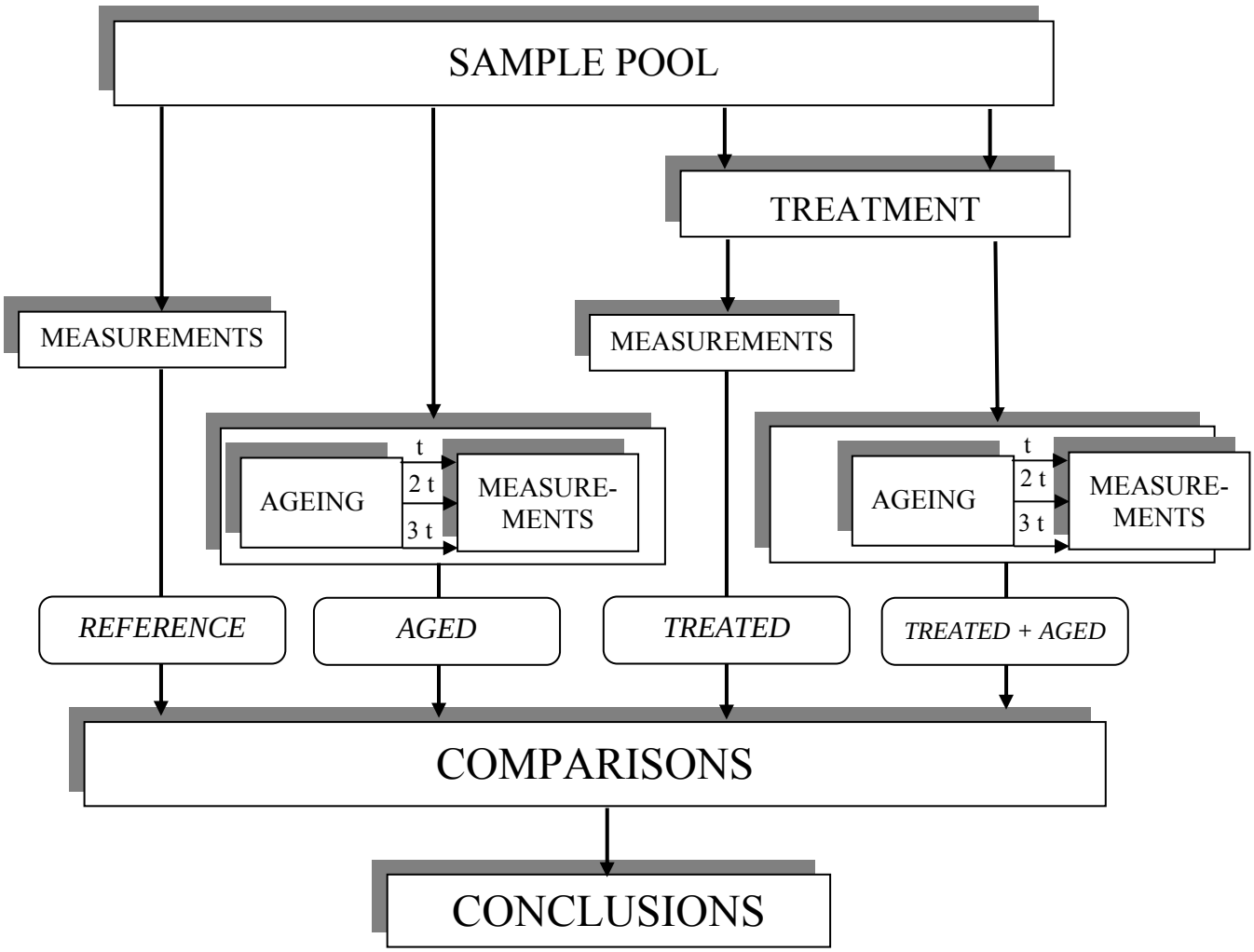

Figure 1: Flow chart of the experimental setup

The samples consisted of various types of paper, as shown in table 2. This table has been published before[11], but this new version includes two more sample series and certain values have been updated with the results of more measurements. The Whatman paper was acquired in 46 cm x 57 cm leaves, which were cut in smaller leaves of 23 cm x 28.5 cm (the larger dimension was parallel to the machine direction of paper) and than in strips of length equal to the leave height (or width in case of CD orientation) and width of 15±0,1 mm. The historical samples were of about A4 dimensions (20x30 cm).

Table 2: Description of the samples. * Mean of all determination of Whatman samples W, X, U

Origin	Code	Fibre	Sizing	pH	Thickness (µm)	Grammage (g/m^2)
Contemporary (Whatman No2)	W, X, U, Y	Cotton	Unsized	7.06*	190	103
ca. 1650	A	rag	Gelatin	8.61	139	70
ca. 1750	B	rag	Gelatin	4.40	213	180
ca. 1700	C	rag	Gelatin	6.74	152	68
ca. 1940	F	Chemical pulp	Rosin	5.78	110	76
ca. 1960	G	Chemical pulp	Rosin	5.41	125	77
1935	K	Mechanical pulp	Rosin	4.80	118	
1954	L	Mechanical pulp	Rosin	5.09	125	

The coding of the samples and their treatments, the ageing times and the setup used for each series are shown in table 3. The results of the sample series W were not used for the evaluation and are not presented here. These samples were not preconditioned before mechanical

testing, thus producing erroneous results. Nevertheless, they indicated that much longer ageing times were necessary to produce significant changes to the mechanical properties of Whatman paper. Sample series W, X, F and G were treated and aged as whole leaves, while the rest of the samples as strips, which were distributed randomly among the various treatments and durations of ageing. This later setup was chosen in order to compensate for the sample inhomogeneity[11]. All samples were aged in sealed vessels at 80°C and 75%RH, except where otherwise indicated (table 3). A detailed description of the sample preparation and the ageing procedure has been presented elsewhere[6, 11, 12]. The sample series Y consisted of Whatman paper, which was aged for 120 days at 75°C and 75%RH prior to treatments, in an attempt to simulate in a reproducible fashion old paper by preaging a contemporary standard paper.

Table 3: Description and coding of the samples and their treatments. Ageing intervals are expressed in days. R: Reference (untreated), H: washed, C: deacidified, M: consolidated, C+M: simultaneous deacidification and consolidation. MD: machine direction, CD: cross direction.

Origin	Code	Ageing (Days)	Treatments	Direction	Setup (quantity)
Contemporary (Whatman No2)	W	0-7-14-21	R-H-C-M	MD+CD	Whole leaves (80 leaves)
Contemporary (Whatman No2)	X	0-40-80-120-160-240	R-H-C-M	MD+CD	Whole leaves (80 leaves)
Contemporary (Whatman No2)	U	0-30-60-90-120-150	R-C	CD	Strips
Contemporary (Whatman No2)	Y	0-34	R-H-C-C+M	CD	Strips
ca. 1650	A	0-25	R-H-C-M	CD	Strips (22 leaves)
ca. 1750	B	0-15	R-C	CD	Strips (6 leaves)
ca. 1700	C	0-25	R-C	CD	Strips (8 leaves)
ca. 1940	F	0-6 (dry oven, 105ºC)	R-C	CD	Whole leaves
ca. 1960	G	0-6 (dry oven, 105ºC)	R-C	CD	Whole leaves
1935	K	0-7	R-C	MD+CD	Strips
1954	L	0-7	R-C	MD+CD	Strips

The following details about the ageing method used here were considered of practical importance:

- The sealing of the vessels was accomplished by a flexible ring, which was held in place by a spring mechanism, embedded on the vessel. The choice of the sealing material is critical. Preliminary ageing experiments indicated that the original rubber sealing ring was unsuitable, since it developed an odour, changed colour and became stiff after 5 days of ageing at 80°C. Silicon rubber was tested, and after 25 days of ageing at 80°C there was no detectable change in weight, colour and mechanical properties. This material was finally chosen for sealing and even after the longest ageing experiment (240 days) it remained unaffected.
- The sealing must be perfect, otherwise the volatile paper products would escape uncontrollably, thus affecting the repeatability of the experiment[11].
- In parallel experiments that involve comparisons, the quantity of the paper and the solution, used for the adjustment of RH, should be the same in all the vessels.
- Preconditioning the samples at the RH of ageing is recommended. It can be accomplished by maintaining the sealed vessels as prepared for ageing at ambient temperature for 24 hours.

RESULTS

The results of the measurements are presented in tables 4 and 5. Standard deviation data can be found in the discussion chapter. The values of the most important properties of the samples are graphically presented in figure 2.

Table 4: Properties of Whatman X Samples. R: Reference, H: Washed, C: Deacidified, M: Consolidated. CD: Cross Direction, MD: Machine Direction. FE: Folding Endurance, TS: Tensile Strength (N/m), TEA: Tensile Energy Absorption (N/m^2), SAB: Streatch at Break (%), L*, a*, b*: Coordinates of the CIEL*a*b* colour system, Wi: Whiteness Index, Yi: Yellowness index, B: Brightness, M%: moisture content %, DP: Degree of Polymerization, δ%: percentage of the hydrolyzed glycosidic bonds.

	FE		TS		TEA		SAB		L*	a*	b*	Wi	Yi	B	pH	M%	DP	δ%
	CD	MD	CD	MD	CD	MD	CD	MD										
XRo	1.34	1.36	1790	2568	39.4	22.2	2.72	1.42	97.64	-0.19	1.77	84.65	2.90	92.47	7.03	5.94	1810	0.000
XHo	1.29	1.36	1542	2089	44.6	30.7	3.73	2.09	97.74	-0.19	1.54	85.28	2.80	92.74	7.32	6.05	1633	0.000
XCo	1.27	1.38	1550	2023	44.5	28.5	3.83	2.07	97.65	-0.20	1.53	85.78	2.59	92.76	9.79	6.06	1713	0.000
XMo	2.05	2.16	2510	3408	84.0	63.5	5.03	3.09	97.60	-0.19	1.66	84.91	1.90	92.36	7.15	6.06	1639	0.000
XR40	1.30	1.39	1722	2537	37.0		2.76	1.41	95.39	0.26	3.52	70.28	6.60	85.45	6.80	5.77	1437	0.029
XH40	1.28		1612		42.6		3.40		95.43	0.28	3.29	70.35	6.52	85.36	6.61	5.82	1142	0.053
XC40	1.27		1492		37.3		3.30		95.74	0.22	3.12	72.65	5.97	86.45	9.59	5.76	1408	0.025
XM40	2.12		2537		85.4		4.49		95.49	0.20	3.33	70.50	6.58	85.58		5.77	1196	0.045
XR80	1.21	1.32	1772	2525	30.5	24.7	2.45	1.47	91.97	0.81	5.79	51.30	11.92	75.14	6.08	5.64	974	0.095
XH80	1.17	1.21	1573	2038		21.0	3.19	1.63	91.92	0.92	5.92	51.92	11.70	75.29	5.75	5.68	739	0.148
XC80	1.23	1.35	1547	2120	36.2	28.7	3.28	1.86	92.52	0.76	5.37	54.04	11.08	76.49	9.17	5.72	938	0.097
XM80	1.97	1.90	2427	2963	75.9	44.7	3.90	2.39	92.41	0.76	5.54	53.02	11.37	75.99	5.98	5.67	839	0.117
XR120	1.08	0.96	1775	2531	32.4		2.39	1.25	87.75	1.79	8.50	31.62	18.79	63.36	5.46	5.41	499	0.291
XH120	0.68		1395		20.8		2.02		87.08	2.02	8.89	29.88	19.42	62.07	5.27	5.20	392	0.388
XC120	1.10		1472		31.0		2.77		89.05	1.47	7.88	35.22	17.35	66.17	8.90	5.43	578	0.229
XM120	1.15		1978		36.3		2.52		88.15	1.72	8.35	34.10	17.68	64.87	5.56	5.32	395	0.385
XR160	0.00	0.00	1214	1469	7.0	4.1	0.88	0.54	83.65	3.02	11.69	15.49	26.02	53.74	4.50	4.74	257	0.667
XH160	0.00	0.00	854	1188	4.0	3.5	0.71	0.50	84.37	2.82	11.34	16.63	25.33	54.37	4.42	4.69	232	0.741
XC160	0.83	0.82	1414	1757	21.7	14.4	2.02	1.22	86.65	1.95	9.71	26.01	20.95	60.61	8.77	5.34	447	0.330
XM160	0.00	0.00	1342	1658	7.7	6.2	0.93	0.68	84.87	2.64	11.04	19.35	24.18	56.55	4.45	4.96	284	0.582
XR240	0.00	0.00	651	887	1.4	1.2	0.36	0.33	76.23	4.52	14.45	0.68	34.61	39.88	4.12	4.31	185	0.972
XH240	0.00	0.00	518	590	0.9	0.9	0.34	0.28	77.51	4.11	13.47	4.08	32.28	42.35	4.21	4.22	184	0.967
XC240	0.14	0.06	892	1241	3.9	4.1	0.73	0.63	79.80	3.58	13.85	4.54	31.61	45.83	7.82	4.62	285	0.585
XM240	0.00	0.00	496	592	0.8	0.7	0.27	0.29	78.40	3.92	13.23	5.86	31.14	44.08	4.19	4.29	187	0.948

Table 5: Properties of Sample series U (Whatman), Y (simulated historical paper) and A, B, C, F, G, K, and L (historical paper). For symbol explanations, see table 4.

	FE	TS	TEA	SAB	L*	a*	b*	Wi	Yi	B	pH	M%	DP	δ%
URo	1.31	1770	37.5	2.60	97.63	-0.11	2.10	82.30	3.73	91.93	7.23	5.58	1810	0.000
UCo	1.30	1593	47.4	3.65	97.68	-0.17	1.74	84.38	3.00	92.30	9.52	5.79	1784	0.000
UR30	1.31	1813	39.0	2.72	96.18	0.23	3.22	72.73	6.15	87.12	6.95	5.43	1587	0.016
UC30	1.28	1617	41.7	3.38	96.54	0.10	2.88	75.60	5.40	88.58	9.33	5.79	1591	0.014
UR60	1.31	1795	36.0	2.58	94.56	0.46	4.11	64.83	8.10	82.65	6.58	5.47	1266	0.047
UC60	1.24	1661	43.8	3.40	94.81	0.39	3.89	66.78	7.58	83.55	9.27	5.45	1276	0.045
UR90	1.22	1760	33.9	2.48	92.20	0.86	5.79	51.87	11.73	75.43	6.08	5.35	845	0.126
UC90	1.23	1597	37.0	2.99	92.80	0.77	5.17	56.32	10.40	77.87	9.22	5.42	1038	0.081
UR120	0.91	1661	25.9	2.09	88.43	1.67	8.56	34.20	17.73	65.28	5.06	5.19	472	0.313
UC120	1.06	1505	27.2	2.37	91.11	1.08	6.32	46.98	13.23	72.57	8.89	5.36	618	0.212
UR150	0.04	1161	6.1	0.89	84.11	2.88	12.02	15.23	26.12	54.93	4.30	4.73	277	0.612
UC150	0.73	1291	11.6	1.48	88.91	1.39	7.98	38.98	15.90	67.63	8.37	5.17	445	0.338
YRo	1.25	1794	35.1	2.43	90.69	1.10	7.09	42.75	14.88	71.15	5.92			
YHo	1.19	1659	37.0	2.88	91.07	1.13	6.55	45.63	13.80	72.15	6.48			
YCo	1.17	1677	39.5	3.03	92.18	0.98	5.94	51.27	12.22	75.35	9.54			
YC+Mo	1.76	2436	62.5	3.22	91.52	1.02	6.08	48.67	12.82	73.65	9.63			
YR34	0.61	1621	22.7	1.86	85.30	2.33	9.81	23.97	21.77	57.93	5.26			
YH34	0.40	1345	13.8	1.56	87.48	1.71	8.38	32.62	18.15	63.48	5.40			
YC34	0.99	1606	28.2	2.36	88.84	1.40	7.40	39.53	15.73	68.02	9.26			
YC+M34	1.45	2397	47.5	2.80	89.82	1.26	7.15	43.43	14.35	70.28	9.42			
ARo	2.79	1842	62.1	4.43	90.36	0.26	10.19	28.74	19.65	68.59	8.61			
AHo	2.78	1734	66.1	5.12	90.71	0.34	8.67	36.04	16.86	70.28	9.21			
ACo	2.64	1706	57.4	4.64	90.90	0.33	8.45	36.97	16.48	70.61	9.43			
AMo	2.99	2156	80.3	4.98	90.03	0.41	9.56	31.24	18.48	67.93	9.14			
AR25	2.30	1703	48.4	3.65	86.61	1.69	14.36	7.33	28.99	57.42	8.41			
AH25	2.34	1624	46.0	3.80	88.27	1.06	12.12	17.82	24.16	62.32	8.65			
AC25	2.23	1590	48.7	4.17	88.64	0.96	12.07	18.16	24.01	63.00	9.18			
AM25	2.60	1826	51.4	3.72	87.84	1.01	12.60	15.82	24.96	61.72	8.92			
BRo	1.80	4642	133.7	3.75	86.27	-0.06	14.86	5.09	28.51	56.80	4.40	6.71	522	0.000
BCo	1.92	3567	104.4	3.86	88.22	-0.52	11.34	21.92	21.15	63.42	9.52	6.44	555	0.000
BR15	0.48	4336	76.9	2.40	77.94	3.62	19.89	-16.00	43.57	38.72	4.28	6.00	355	0.179
BC15	1.54	2820	63.7	2.98	86.64	0.20	14.89	6.22	28.27	57.68	8.18	5.94	490	0.047
CRo	2.31	1834	57.7	4.09	91.19	-0.39	11.37	24.18	21.13	69.26	6.74	6.39	981	0.000
CCo	1.90	1491	46.2	4.20	92.82	-0.07	8.04	42.10	15.17	75.63	9.36	6.40	1024	0.000
CR25	1.53	1393	20.7	2.03	80.39	3.72	17.74	-9.17	39.19	43.71	5.79	5.76	562	0.152
CC25	1.63	1195	22.3	2.54	88.64	1.46	12.65	15.64	25.42	62.16	8.27	5.92	815	0.050
FRo	1.30	1050	20.3	2.43	87.93	0.99	13.84	10.46	27.13	60.53	5.78			
FCo	1.32	992	24.5	3.00	88.81	0.77	12.89	14.80	25.32	63.09	8.89			
FR6	0.93	984	13.4	1.83	86.40	1.63	16.47	-0.89	32.57	55.68	5.94			
FC6	1.29	904	14.3	2.03	87.50	1.49	15.72	2.73	30.88	58.19	8.74			
GRo	1.23	1104	18.0	2.13	91.53	-0.10	15.17	7.93	27.66	65.70	5.41			
GCo	1.29	1082	26.0	3.04	91.21	0.23	13.85	12.84	26.00	66.06	8.83			
GR6	1.09	1112	20.8	2.36	90.46	0.32	16.00	1.34	30.60	62.34	5.29			
GC6	1.22	1072	23.8	2.88	90.68	0.47	15.24	8.84	27.67	64.22	8.73			
KRo	0.54	910	6.4	1.11	78.47	4.27	21.57	-20.45	47.02	38.84	4.80			
KCo	0.62	848	7.7	1.46	77.34	3.28	21.62	-21.32	46.55	38.25	8.61			
KR7	0.34	892	6.1	1.12	74.47	4.94	21.86	-21.43	49.47	33.43	4.59			
KC7	0.58	773	5.8	1.32	76.09	4.09	22.59	-23.37	49.05	35.75	8.33			
LRo	0.28	802	7.4	1.35	87.31	-0.22	14.09	9.44	26.63	59.88	5.09			
LCo	0.35	817	9.4	1.67	85.94	-0.50	15.84	1.42	29.85	56.18	8.72			
LR7	0.24	860	8.3	1.45	85.26	1.10	14.69	4.03	29.93	54.65	4.79			
LC7	0.28	815	7.9	1.50	85.30	-0.04	17.07	-3.80	32.57	53.82	7.90			

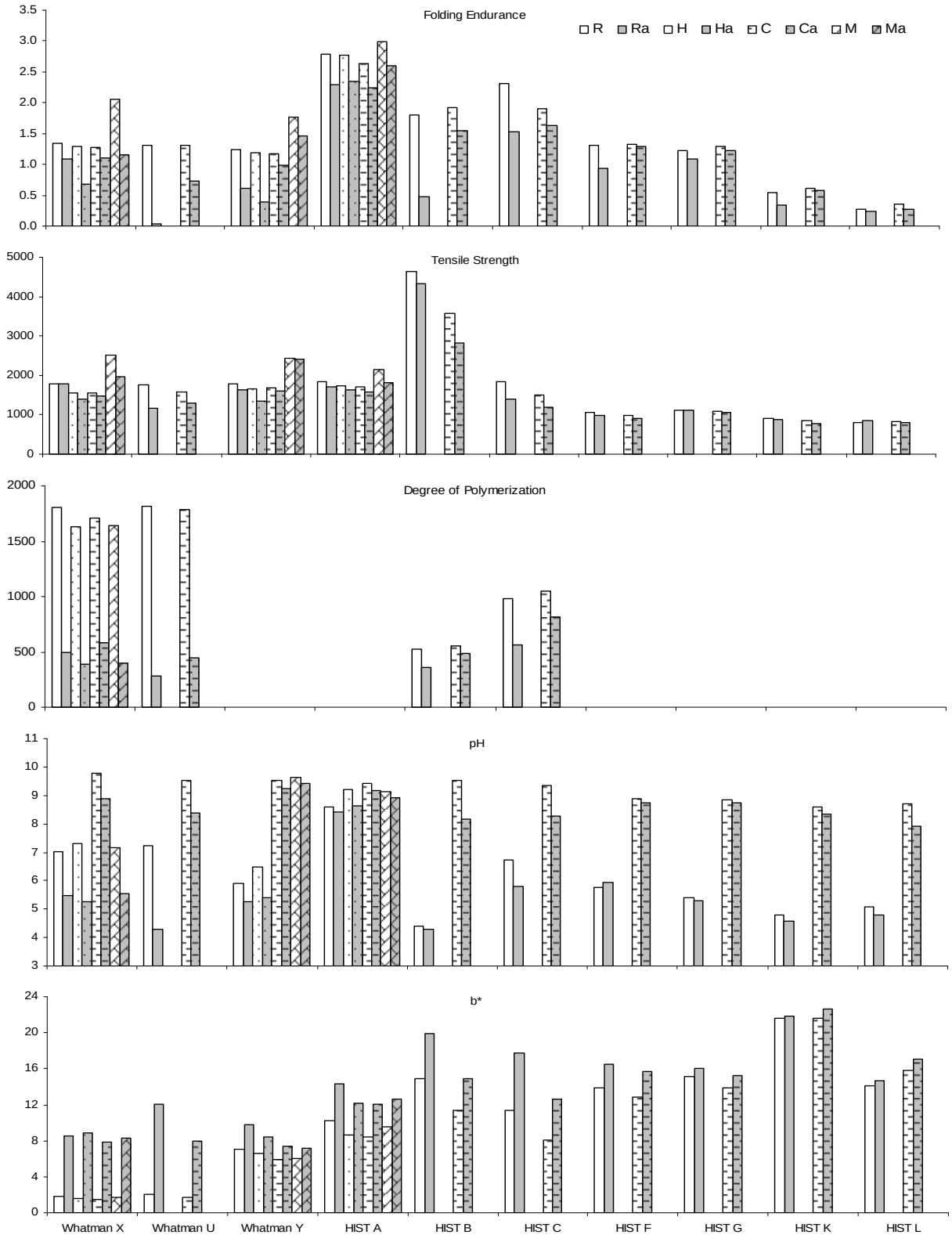

Figure 2: Values of the most important properties of all sample series. R: Reference, H: Washed, C: Deacidified, M: Consolidated. The subscript *a* stands for *aged*. The property values of the aged samples of series X and U presented here correspond to 120 and 150 days of ageing respectively. TS in N/m.

DISCUSSION

Statistical correlation among paper properties

Correlations between variables can be studied by many statistical tools, the simplest and most straightforward of all being the correlation coefficient (r). The correlation coefficient can be calculated by a statistical program (or Microsoft Excel®) and varies between -1 and 1. A value of r close to 1 indicates a very strong positive correlation (that is, both variables increase proportionally) and a value close to -1 a very strong negative correlation (that is, when one of the variables increase, the other decreases inversely proportionally). Values of r around zero indicate no correlation. Accordingly, the mean values of the various sample properties (untreated, treated, untreated and aged, and treated and aged) were tabulated (tables 4, 5) and the correlation coefficient between any pair of them was calculated. In case that two or more properties are strongly correlated, the determination of all of them in such a study is not necessary. The easiest and most conveniently determinable suffices, with the consequent result of time, resources and sample saving. The statistical correlation of two seemingly unrelated properties could also signify a subtle but fundamental interdependence between them.

Table 6. Correlation coefficients of the properties of all sample series. For symbol explanations, see table 4.

Property	FE	TS	TEA	SAB	L*	a*	b*	Wi	Yi	B	pH	M%	DP	δ%
FE	1	0.514	0.777	0.892	0.520	-0.574	-0.302	0.327	-0.372	0.459	0.554	0.865	0.586	-0.869
TS	0.514	1	0.824	0.454	0.270	-0.333	-0.245	0.253	-0.272	0.268	0.086	0.692	0.103	-0.536
TEA	0.777	0.824	1	0.841	0.450	-0.535	-0.351	0.373	-0.399	0.434	0.315	0.810	0.334	-0.670
SAB	0.892	0.454	0.841	1	0.678	-0.703	-0.479	0.518	-0.549	0.637	0.595	0.882	0.678	-0.884
L*	0.520	0.270	0.450	0.678	1	-0.856	-0.853	0.888	-0.916	0.981	0.451	0.580	0.900	-0.796
a*	-0.574	-0.333	-0.535	-0.703	-0.856	1	0.562	-0.598	0.676	-0.780	-0.490	-0.787	-0.775	0.877
b*	-0.302	-0.245	-0.351	-0.479	-0.853	0.562	1	-0.983	0.988	-0.923	-0.296	-0.267	-0.833	0.538
Wi	0.327	0.253	0.373	0.518	0.888	-0.598	-0.983	1	-0.979	0.958	0.334	0.359	0.902	-0.614
Yi	-0.372	-0.272	-0.399	-0.549	-0.916	0.676	0.988	-0.979	1	-0.961	-0.351	-0.372	-0.851	0.625
B	0.459	0.268	0.434	0.637	0.981	-0.780	-0.923	0.958	-0.961	1	0.425	0.510	0.922	-0.739
pH	0.554	0.086	0.315	0.595	0.451	-0.490	-0.296	0.334	-0.351	0.425	1	0.468	0.549	-0.619
M%	0.865	0.692	0.810	0.882	0.580	-0.787	-0.267	0.359	-0.372	0.510	0.468	1	0.546	-0.899
DP	0.586	0.103	0.334	0.678	0.900	-0.775	-0.833	0.902	-0.851	0.922	0.549	0.546	1	-0.741
δ%	-0.869	-0.536	-0.670	-0.884	-0.796	0.877	0.538	-0.614	0.625	-0.739	-0.619	-0.899	-0.741	1

Table 7. Correlation coefficients of the properties of Whatman sample series (X, U and Y). For symbol explanations, see table 4.

Property	FE	TS	TEA	SAB	L*	a*	b*	Wi	Yi	B	pH	M%	DP	δ%
FE	1	0.834	0.925	0.856	0.838	-0.862	-0.842	0.810	-0.850	0.827	0.585	0.887	0.745	-0.894
TS	0.834	1	0.754	0.544	0.692	-0.717	-0.662	0.622	-0.688	0.658	0.402	0.796	0.583	-0.798
TEA	0.925	0.754	1	0.943	0.771	-0.782	-0.779	0.758	-0.782	0.766	0.514	0.823	0.702	-0.790
SAB	0.856	0.544	0.943	1	0.882	-0.892	-0.887	0.864	-0.891	0.875	0.617	0.929	0.776	-0.893
L*	0.838	0.692	0.771	0.882	1	-0.995	-0.990	0.980	-0.995	0.994	0.583	0.946	0.916	-0.967
a*	-0.862	-0.717	-0.782	-0.892	-0.995	1	0.985	-0.968	0.993	-0.986	-0.607	-0.958	-0.896	0.979
b*	-0.842	-0.662	-0.779	-0.887	-0.990	0.985	1	-0.994	0.997	-0.996	-0.583	-0.938	-0.942	0.948
Wi	0.810	0.622	0.758	0.864	0.980	-0.968	-0.994	1	-0.988	0.995	0.568	0.919	0.965	-0.927
Yi	-0.850	-0.688	-0.782	-0.891	-0.995	0.993	0.997	-0.988	1	-0.996	-0.589	-0.946	-0.926	0.960
B	0.827	0.658	0.766	0.875	0.994	-0.986	-0.996	0.995	-0.996	1	0.580	0.935	0.947	-0.951
pH	0.585	0.402	0.514	0.617	0.583	-0.607	-0.583	0.568	-0.589	0.580	1	0.627	0.596	-0.685
M%	0.887	0.796	0.823	0.929	0.946	-0.958	-0.938	0.919	-0.946	0.935	0.627	1	0.826	-0.953
DP	0.745	0.583	0.702	0.776	0.916	-0.896	-0.942	0.965	-0.926	0.947	0.596	0.826	1	-0.848
δ%	-0.894	-0.798	-0.790	-0.893	-0.967	0.979	0.948	-0.927	0.960	-0.951	-0.685	-0.953	-0.848	1

Table 6 presents the correlation coefficients calculated from all the samples, while Table 7 the ones calculated from Whatman paper only (sample series X, U, and Y). The study of the tables led to the following conclusions:

- The optical parameters L*, b*, Wi and Yi appear to be very strongly intercorrelated, especially in the case of the more homogenous population of Whatman paper samples (table 7).
    - Parameters L* and B exhibit very strong positive correlation (r=0.981). The correlation is nearly perfect for the Whatman series. Since both parameters measure brightness, such a result was expected.
    - Very strong statistical correlation is exhibited between b* and Wi (negative correlation, r=-0.983), and b* and Yi (positive correlation, r=0.988). These results were also expected, since the increase of b* and Yi signify the intensification of yellowness and the decrease of whiteness (Wi).
- The optical parameters exhibit relatively strong correlation to DP and δ%, especially for the Whatman samples. This observation reconfirms that optical properties are related to the chemistry of the samples.
- From the mechanical properties, FE exhibits strong correlation to TEA and SAB. Intermediate correlation appears to exist between TEA on the one hand and TS and SAB on the other, which was predictable, since Work is defined as Force times Space (W = F x S). The mechanical properties except from TS exhibit a relatively strong correlation to moisture content (M%) and FE and SAB are negatively correlated to δ%. All corresponding correlation coefficients are higher for the Whatman samples. The strong correlation of FE and SAB to δ% indicates that from the mechanical properties tested here, these two are the most sensitive to the chemical decay which occurs due to accelerated ageing and that they are related more strongly to the chemistry of the samples than the other mechanical properties.
- From the properties tested, none is strongly correlated to pH. The stronger correlation to pH is exhibited by δ%, FE and SAB, especially for the Whatman samples. This observation lends further support to the tenet that the decay of cellulose during thermal accelerated ageing is pH dependent (mainly acid hydrolysis). This result also indicates the stronger dependence of FE change on pH.
- Most of the examined properties appear to correlate better to δ% instead of DP. Thus, δ%, except from facilitating the kinetic study of the decay[6, 12], appears to be a more suitable and descriptive variable than DP for monitoring the changes induced to cellulose by conservation and ageing.

Evaluation of the suitability of tested properties

Mechanical properties

The experimental results indicated that FE is the most sensitive mechanical property for the detection of the changes induced to the samples by accelerated ageing. 40 days of ageing were sufficient to induce detectable changes to the FE of the Whatman samples, while TS was affected after 120 days of ageing. The following table (table 8) presents the loss of the mechanical strength of the historical samples A, B and C in relation to their pH and the duration of ageing. It is apparent that the sensitivity of FE in registering changes increases as pH decreases.

Table 8: Mechanical strength loss of the historical samples A, B and C in relation to their pH and duration of ageing

Sample Series	pH	Days of Ageing	FE Loss (%)	Fold Number Loss (%)	TS Loss (%)	SAB Loss (%)	TEA Loss (%)
A	8.61	25	18	66.5	7.5	17.6	22
C	6.74	25	34	83	24	50	64
B	4.40	15	73	95	6.6	36	42.5

Moreover, folding endurance revealed differentiations of the sample behaviour according to their conservation treatment. The immediate impact of the treatments on FE varies with the sample series. Contrary to the commonly expressed opinions, the increase of FE after aqueous treatments is not the rule[11].

The unique feature that qualifies FE as the most significant mechanical property as far as the evaluation of paper conservation interventions is concerned, is its direct connection with paper usability. The statement that a paper exhibiting high values of FE is more usable than another with lower values sounds reasonable, but the same can be argued for paper having higher values of tensile strength or other mechanical properties. That is, it can be argued that the higher the values of any mechanical property, the more usable the paper is. However, by comparing the mechanical properties of Whatman paper, it is apparent that when FE drops to zero, all the other mechanical properties retain a considerable portion of their initial values (table 9). Since paper having zero value of FE cannot withstand folding without sustaining serious damage, it cannot be used as an information carrier. Thus, when FE drops to zero, although the other mechanical properties have not, paper ceases to be usable. There is no other paper property possessing this feature. In fact, paper stops being usable before FE reaches zero, since it is not trustworthy if it cannot withstand at least a few folds, but this fact does not reduce the value of the above mentioned observation.

Table 9: Mechanical strength retained (%) after 40, 80, 120, 160 and 240 days of ageing (untreated Whatman paper, sample series XR, CD)

Mechanical Property	0	40	80	120	160	240
FE	100	97	91	81	0	0
TS	100	96	99	99	68	36
SAB	100	101	90	88	32	13
TEA	100	94	78	82	18	3

There is one drawback inherent to FE determination: historical paper suffering advanced natural decay (weak, brittle or molded paper) very often cannot withstand folding, thus resulting zero or very low values of FE (see FE results of sample series L). More flexible design of the folding endurance testing apparatus, allowing for the adjustment of tension to very low values or for decreasing the folding angle could compensate for this drawback. A thus modified instrument was described by Barrow et al.[13], but such an instrument is not easily available. Nevertheless, since conservation methods are never tested on the original material and the choice of samples is

in the researcher's decision, paper having adequate strength can be used, eliminating thus the above mentioned drawback.

But the most important drawback of the FE determination is the significant scatter of the results. The standard deviation of the sample series Whatman U was 6.9% for the untreated samples and ascended to 15.4% for the aged for 120 days samples. The standard deviation of the UC120 samples (Whatman U, deacidified, aged for 120 days) was 13.2%, and the lowest value of folds was 4 while the highest was 22, five times greater than the lowest. Conservation treatments and ageing tended to raise the values of standard deviation, since small differences among the samples were enhanced by presumable spatial fluctuations of the temperature in the ageing oven and inevitable minor differences (in handling, drying and duration) among the treatments of the different paper leaves or strips of the same sample series. The historical samples exhibited higher values of standard deviation of the FE measurements. This was expected since natural ageing might have enhanced minor initial differences among different leaves, but also because handmade paper is far more inhomogeneous than Whatman paper, which is manufactured according very strict standards and with great care. For example, the standard deviation of the HIST ARo samples was 9.3% and of the AM25 12.2%. In an attempt to decrease the scatter of the results, all the available paper was used and the maximum possible measurements were taken. The relevant ISO standard prescribes 10 measurements per sample. In this study and for the Whatman U sample series, the measurements per sample were around 40, while for HIST A between 10 and 25, depending on the paper availability and the number of the rejected measurements.

The results reconfirmed that tensile strength (TS) is relatively insensitive towards accelerated ageing and that its sensitivity is not consistent throughout the duration of ageing. During the first half of the duration of ageing, the change of TS is not statistically significant, while in the next 40 days of ageing a statistically significant change is manifested (table 9). The minor increase observed in the TS of the U samples at the initial stage of ageing has been also reported by other researchers and has been attributed to the crosslinking of the cellulose molecules[14]. It was verified experimentally that TS was significantly affected by aqueous treatments, its decrease being the rule[11]. This sensitivity of TS could be exploited for the detection of the immediate impact of immersion and wetting treatments with water and probably other solvents.

By comparing the TS results to those of FE of the Whatman X sample series, it is further verified that TS is not a sensitive criterion of the sample usability. The TS of the C240 samples is marginally greater than that of the H160 samples, but the C240 samples retain some folding capability while H160 do not. The difference in the TS of the R160 and C160 samples is insignificant, but C160 samples withstand 7 folds and are usable, while R160 retains no folding ability and collapse. The resolution of the TS concerning paper usability is low. Relatively small changes of TS result in a total loss of usability. These conclusions are in agreement with the relevant literature and manifest that FE is a better criterion of paper usability than TS.

Stretch at Break (SAB) and Tensile Energy Absorption (TEA) are more sensitive than TS but less than FE (table 9), and manifested differences induced to the samples by ageing and conservation treatments. These methods provide about the same information and can substitute each other. They are supposed to better connect to paper usability than TS: higher SAB and TEA indicate greater ability of deformation and higher capability of work absorption respectively before failure. Nevertheless, it is doubtful whether a paper under normal usage conditions is ever exposed to such tensile stresses that can bring about its failure.

Cold extraction pH

According to the previous discussion, FE loss can be used as a reliable and sensitive index of paper stability. Table 8 was used to show the dependence of the sensitivity of FE change with accelerated ageing on pH, but if read differently, it also shows that pH can serve as a paper stability index towards accelerated ageing.

Table 10 demonstrates the pH dependence of a composite index based on the FE loss. This index is equal to the ratio of the FE change of the reference over that of the deacidified sample, both aged for the same period ($\Delta FE_R/\Delta FE_C$), and reflects the improvement of the ageing resistance of the samples due to deacidification.

Table 10: $\Delta FE_R/\Delta FE_C$ %, $\Delta DP_R/\Delta DP_C$ % and pH of the sample series A, U, B and C.
* FE and DP values correspond to 150 and 120 days of ageing respectively.

Sample Series	pH	$\Delta FE_R/\Delta FE_C$ %	$\Delta DP_R/\Delta DP_C$ %
A	8.61	120	-
U	7.23	223*	115*
C	6.74	288	200
B	4.40	347	256

It is apparent that acidic samples benefit the most from deacidification. Thus, pH determines the effectiveness of the treatment and at the same time can serve as an index of the chemical stability of the samples. Alongside, is can be used as a criterion for the application of deacidification. Since non acidic samples do not benefit considerably from deacidification and taking into consideration that their mechanical properties might be negatively affected[11], it is plausible that deacidification should not be applied to non acidic papers if aqueous treatments are not necessary for other reasons (for example, for the removal of stains that disfigure art-work on paper).

The pH decrease and its final value after accelerated ageing facilitate the evaluation of the stability and the adequacy of the alkali reserve. The large quantity of the required paper (2x2 g. for both determinations prescribed in the standard) is a serious drawback of the method. If caution is exercised so that paper is not contaminated, the paper used for the determination of the mechanical properties can be reused for the pH determination. Thus, mechanical tests should precede the chemical tests. The standard deviation of the pH determination was low and did not exceed 1.1%.

Degree of Polymerization (DP)

The determination of the DP of cellulose of the sample papers was the most sensitive method for the detection of changes induced by accelerated ageing. The transformation of the DP to δ% values facilitated the kinetic study of paper ageing[6]. DP determination is feasible for papers that consist of (almost) pure cellulose (papers made of rag, cotton linters, or chemical pulp). The application of the method to paper that contains more than traces of lignin (paper made of various mechanical pulps) was not attempted, since it would introduce considerable errors due to the insolubility of the lignin component to the used solvents. The repeatability of the method was very good, since the standard deviation of the DP determination varied around 1.3% and never exceeded 2.2%. The method is relatively expensive (the solvent is costly) and time consuming. The solvent is toxic to human and detrimental to the marine life and must be discarded according to the relevant regulations.

Fourier Transform Infra-Red Spectroscopy (FTIR)

Infra-red Spectroscopy was proved to be an excellent method for the detection of additives (gelatine and kaolinite) in historical and contemporary papers (figures 3, 4). It facilitated the semi-quantitative determination of the gelatine content of historical papers, thus permitting the monitoring of the diminishing effect of the aqueous conservation treatment on it[11]. FTIR detected lignin, permitting the discrimination between mechanical and chemical pulps (figure 3). No evidence of crosslinking was found in the spectra of aged papers.

Since oxidation evokes the production of carbonyls that absorb at the 1720-1735 cm^{-1} region, the recording of this area of the IR spectrum of paper facilitates the estimation of the extent of oxidation. In figure 3, the spectrum of the KRo sample is shown. The spectrum exhibits

a peak of strong absorption at 1734 cm^{-1}, which according to the previous discussion indicates extensive oxidation. Aqueous deacidification reduced the intensity of this peak or eliminated it altogether. It has been shown that this peak corresponds to the carbonyl of the protonated carboxyl (-COOH), which only exists at low pH[15, 16, 17]. Deacidification increases the pH of paper and converts the carboxyl to the carboxylate form ($-COO^-$), which according to the relevant literature absorbs at 1618 cm^{-1} [15, 16, 17]. It can be seen that there was no discernible change in the absorption at this region of the spectrum of the deacidified paper (KCo, fig. 3). Therefore, the most plausible explanation for the disappearance of the 1734 cm^{-1} peak from the spectrum of the deacidified paper (KCo) is that it must be associated to the water-soluble, low-molecular mass degradation products of paper components (cellulose, lignin, hemicelluloses and various additives), which were dissolved by the deacidification bath and removed from the paper. Thus, this attribute of the spectra can be used for the evaluation of the effectiveness of washing and aqueous deacidification.

All the above can be accomplished non-destructively and without any sample preparation by FTIR microscopy (μFTIR, figure 4). Nevertheless, FTIR itself can hardly be characterized as a destructive method, since for the pellet preparation a sample of a few mg of paper is adequate.

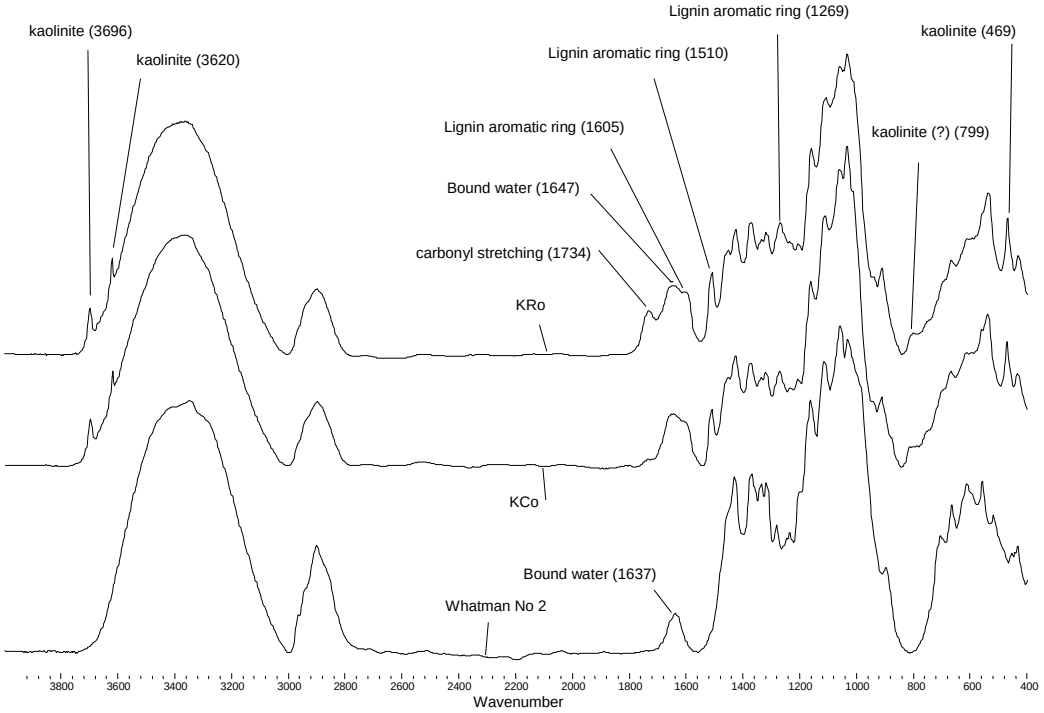

Figure 3: FTIR spectra of Whatman (pure cellulose), KRo and KCo paper (the spectra are displaced vertically for clarity). The absorption bands of kaolinite and lignin are evident. The band at 1734 cm^{-1} in the spectrum of KRo is due to carbonyl stretching, an indication of oxidized and aged paper. This band is absent from the spectrum of the deacidified paper (KCo).

Colorimetry

Colour determination was very sensitive, since it detected changes from the first few days of ageing (7 days, Whatman W). The repeatability of the method was quite good: the standard deviation of L* for the XRo samples was below 0.1% and reached 1% for the XR240 samples, of b* between 4% and 6%, of Wi from 0.2% for the XRo to 15.5% for the XR160, of Yi around 3.5% and of B from 0.1% for XRo to 4% for the XC240 samples. The repeatability was lower for the historical samples, which were less homogenously coloured.

Colorimetry permits the direct and objective aesthetic evaluation of the treatment and is a completely non-destructive method[10]. The increase of lightness (increase of L*, B and Wi) and the decrease of yellowness and redness (decrease of b*, Yi and a*) result in the aesthetic improvement of paper (cleaning, improvement of readability). It is the only method that

facilitates the objective aesthetic evaluation of a conservation treatment and therefore must always be included in relevant studies. The determination of one lightness or one yellowness parameter suffices, the choice of parameter not being critical, but depending on the available instrumentation. A colorimeter functioning in the CIEL*a*b* colour system represents the best choice. The determination of the yellowness index (Yi) is not recommended for yellow papers.

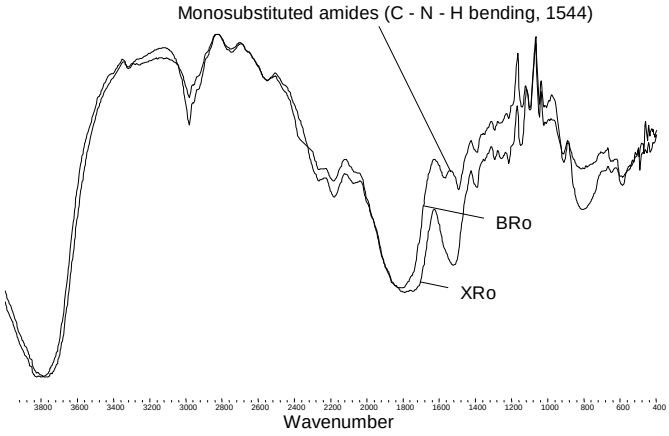

Figure 4: μFTIR spectra of Whatman No 2 (pure cellulose) and BRo paper. The absorption band at 1544 indicates the presence of gelatine.

Chemical changes, such as hydrolysis and oxidation of cellulose itself and its degradation products and lignin oxidation, resulting from natural or accelerated ageing, affect the colour of paper. The produced chromophores absorb the blue component of light, decreasing the lightness of paper and increasing yellowness. Thus, the colour change of the samples reflects the chemistry of degradation, providing information about the extent of the chemical reactions that are responsible for paper ageing. The strong correlation found between colour parameters and δ% supports that aspect. Therefore, the inhibition or the decrease of the color change due to a conservation treatment can be utilized for its evaluation.

Other methods

The other methods discussed briefly below were not used for the evaluation itself but were complimentary methods intended for the clarification of the changes induced by accelerated ageing and conservation. A detailed account of their results will be the subject of a future paper.

- Fibre Optics Microscopy: The FOM images of the area of the tensile failure showed that the aged Whatman samples lacked protruding fibres, which were evident in the reference samples (figure 5). This observation indicated that the tensile failure of the unaged samples occurred mainly because of bond failure among cellulose fibres, while that of the aged samples because of fibre failure. The tensile strength of paper depends on the fibre strength, which is affected by ageing, and on the bond strength among cellulose fibres, which remains practically unaffected by it[18]. Initially, the fibre strength is much higher than that of the bonds and the strength of paper is determined by the strength of the bond. Considering that the tensile strength remained practically unchanged for the first 120 days of ageing but the degree of polymerization was immediately affected (see tables 4, 5, and 9), it is apparent that fibre strength diminished gradually, until it dropped under the bond strength and that the value of the tensile strength at the onset of its decrease should correspond to the bond strength between cellulose fibres. Thus, the absence of protruding fibres serves as an indication of advanced ageing and low fibre strength.
- Degree of crystallinity: It has been a matter of controversy whether ageing affects the degree of crystallinity and if it does, towards what direction[19, 20, 21, 22]. It was established that ageing increases the Crystallinity Index, while the conservation interventions applied here did not affect it.

- Water Vapour Adsorption: Water vapour was used as a structural probe. The method indicated that ageing reduced the water-vapour absorption capability of paper, promoted hornification and resulted in a more compact structure. Aqueous conservation methods had an impact on paper structure, its nature being still under study.
- Moisture Content under standard conditions (M%): The water content of paper is reduced by accelerated ageing. FE, SAB and TEA were found to correlate significantly to M%, but such a correlation is just an indication of ageing and cannot be straightforwardly exploited for evaluation purposes.

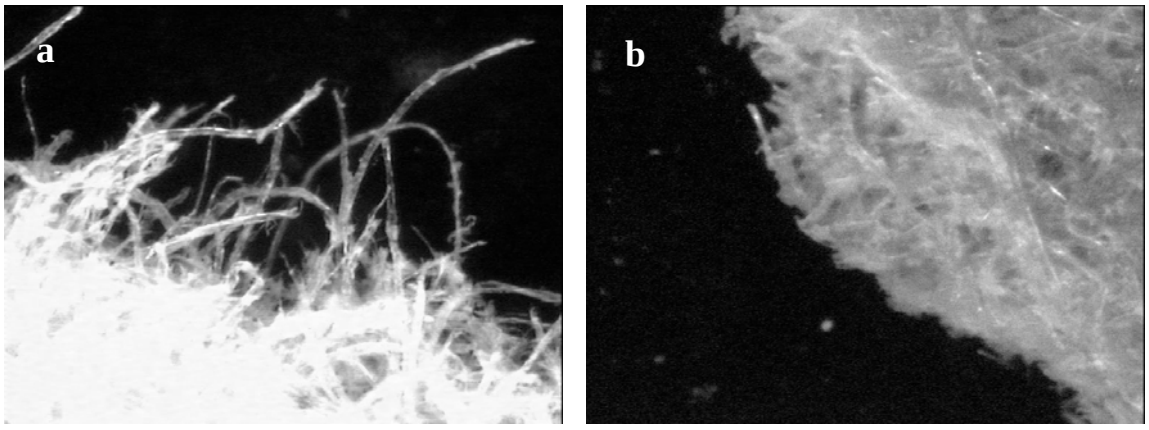

Figure 5: FOM images of reference (a) and aged for 240 days (b) Whatman paper. Magnification X200.

Evaluation of paper conservation treatments

Washing with deionized water

Washing with deionized water was applied to 3 sample series: a contemporary paper consisting of pure cellulose (Whatman X), the same paper which had undergone controlled preageing (Whatman Y) and a truly historical paper (HIST A). The main objective of the treatment was the determination of the impact of the solvent (water) by comparing the properties of the washed to those of the deacidified paper. Washing is a valid conservation treatment, but the use of deionized water is not recommended.

The immediate impact of washing on the FE of X and A samples was insignificant; only the FE of Y samples decreased significantly. Statistically significant was the decrease of TS, while TEA and SAB increased significantly. pH generally increased and the colour of the samples was improved. The change of the colour parameters (increase of L*, B, Wi and decrease of b* and Yi) was statistically significant in all cases. DP was determined only for the X samples and exhibited a statistically significant decrease.

The impact of accelerated ageing was more uniform. It caused an overall deterioration of almost all the properties of the samples X and Y to worse levels than the untreated samples, but definitely worse than those of the samples C, M and C+M. Similarly affected were the mechanical properties of samples A. The colour of the samples AH was better than that of the samples AR and AM+C, but worse than that of the AC samples. The pH of the washed samples was similar to that of the untreated but worse than that of the C, M and C+M samples. The washed samples of the X and Y series deteriorated faster than the untreated samples.

An overview of the results of the washing with deionized water indicates that the benefits of the treatment are meagre and mainly concern the colour improvement of the historical samples. Ageing caused more deterioration to the treated than to the untreated samples. This can be attributed to the dissolution and removal of the traces of Ca^{2+} and Mg^{2+}, originating from the water used for the manufacturing of paper, by deionized water. In the untreated paper, these cations reduced the extent of hydrolysis by neutralizing a part of the acidity of paper that

developed during ageing. Taking into consideration the deterioration of the ageing rate, the insignificant positive results and that with the same infrastructure, cost and labour a more effective treatment could be implemented, washing with deionized water was not regarded as a suitable conservation treatment.

Deacidification with Calcium Hydroxide

The immediate impact of the treatment has been discussed elsewhere[11]. In short, FE and TEA exhibited mixed trends, while TS decreased and SAB increased in all of the cases. These changes were attributed to the action of the solvent (water), since they occurred to the washed samples as well. As far as the impact of the ageing is concerned, in most of the cases the deacidified samples deteriorated at a lower rate than the untreated, washed and consolidated ones. The deacidified samples retained a larger portion of their FE after ageing with the exception of A series, but a smaller portion of their TS than the untreated samples (B, C, F and K). This observation caused considerable bewilderment, but no plausible explanation can be proposed. The other mechanical properties of the samples were generally better after ageing.

The colour of the samples improved after deacidification, the improvement being greater than that of the washed samples. It seems that the alkaline bath of deacidification can dissolve more coloured paper degradation products (which as a rule are acidic) than the slightly acidic deionized water (pH 5.5). Samples K and L (mechanical pulp) were the exceptions to this rule, exhibiting higher yellowness and lower lightness after deacidification. The worsening of the colour of these samples was attributed to lignin oxidation caused by the alkaline bath. Ageing brings about less deterioration to the colour of the samples, K and L excepted, evidently because lignin oxidation prevails, causing greater deterioration to the deacidified samples than to the untreated ones.

The pH of the Whatman and the historical rag papers increased after deacidification to values around 9. Lower increase was observed for the historical papers which were sized with rosin, evidently because of their highly hydrophobic character. The stability of the alkali reserve was satisfactory in all cases, since the pH of the aged samples never dropped bellow 7.

The DP of the Whatman samples decreased after deacidification, the decrease being statistically significant for the sample series X. If the decrease was real and did not originate from experimental errors, it could have been caused by the action of water, because it was observed in all the aqueous treated samples. This matter is still under investigation. The slight increase of the DP of the historical samples must have originated from the removal of the low molecular weight ageing products, which caused a subsequent shift of the DP to higher values. The DP of the deacidified samples decreased less than the untreated and the otherwise treated samples and exhibited a lower rate of bond breaking.

It has been claimed before (table 8, 10) that acidic samples benefit the most from deacidification. Another composite index based on the loss of DP (table 10) supports this opinion. This index equals the ratio of the DP change of the untreated over that of the deacidified sample for the same period of ageing ($\Delta DP_R/\Delta DP_C$) and reflects the improvement of the ageing resistance of the samples because of deacidification.

The preceding discussion confirms that while deacidification improves the ageing resistance of paper, it also has negative results: immediate worsening of TS with lower values after ageing and negative impact on the colour of lignin-containing paper. The colour changes are not that important, since they are not readily perceptible except if treated and untreated papers are observed side by side. As far as the mechanical properties are concerned, because of the close relation of FE to the usability of paper, changes in FE are considered more important than changes in TS. Thus, the outcome of the final evaluation is that deacidification is an acceptable paper conservation treatment but should not be applied indiscriminately. As stated above, only acidic papers should be deacidified, except if aqueous treatments are necessary for other reasons (for example, for the removal of stains that disfigure art-work on paper). Finally, a modification of the treatment that would eliminate its drawbacks would have been desirable.

Consolidation with methylcellulose

Experimental results verified that the treatment with methylcellulose did not induce any undesirable effect on the ageing stability of the samples. Only the colour of the treated samples was in some cases slightly worse than that of the washed samples. Contrariwise, the treated samples had higher strength values for all their useful life, compared to the untreated or otherwise treated samples. The increase in strength was not accompanied by loss of flexibility. On the contrary, FE and SAB that should have decreased if the samples had become more brittle, increased considerably. The DP of the strengthened X samples exhibited a statistically significant decrease, which was attributed to the action of water, since it manifested in the case of the washed samples as well. Therefore, strengthening with methylcellulose solution was accepted as an effective conservation treatment, since it performed according to our expectations by increasing the strength of the samples without inducing any undesirable side effect.

At this point, it should be stressed that these conclusions are valid for the specific type and batch of methylcellulose. The producers and dealers of conservation materials can modify the specifications of their products without indicating that to their customers. The code name and the scant information provided by dealers to conservators about a product are usually insufficient to clarify its composition and properties. Subsequently, retesting is recommended, every time a new batch of the product is purchased.

Simultaneous deacidification and consolidation

Considering the drawbacks of deacidification and consolidation, we decided to try the combined treatment proposed previously by Guerra et al.[23]. Consolidation would eliminate the drawback of the mechanical property decrease observed in all aqueous treatments and deacidification would offer the chemical stabilization that consolidation lacked. Thus, apart from the obvious benefits concerning the conservation of paper, time and resources would be saved. The results of the treatment fully justified our expectations. All the final values of the properties of the samples (Whatman Y) treated this way were higher than the untreated or the otherwise treated samples. In many cases, the values of the properties after ageing were higher than the initial values of the untreated samples before ageing. Thus, the simultaneous deacidification and consolidation represents the ideal aqueous treatment combining the advantages of deacidification (chemical stabilization) and consolidation (mechanical strengthening) and lacking the drawbacks of both.

CONCLUSIONS

Evaluation of the suitability of the tested properties

Concerning the suitability of the methods used for the evaluation of paper conservation interventions, the following conclusions were drawn:

- The most suitable method for the estimation of the mechanical strength of paper is the determination of folding endurance, mainly because of its relation to paper usability but also because of its sensitivity. The low repeatability and the difficulty of the application of the method to weak historical papers are its main drawbacks. Tensile testing can be used for the determination of the immediate impact of the treatments, but not for the investigation of the results of accelerated ageing. The decrease of tensile strength after aqueous treatments seems to relate to damage of bonding among cellulose fibers[11]. Stretch at break and tensile energy absorption can supplement the folding endurance results, but offer no more information. The results of the mechanical tests are almost identical in machine and cross direction (MD and CD, see table 4). Mechanical testing is considered indispensable for conservation evaluation studies because it manifests the effects of the conservation treatment on the usability of paper. It also registers changes that might be invisible to chemical testing. Testing mechanical properties in both machine and cross direction is not necessary, since the results are the same (see table 4).

- The cold extraction pH of paper serves as a crude index of its stability towards accelerated ageing and can be used for the evaluation of the alkali reserve stability and adequacy.
- DP determination applies to lignin-free samples and is very sensitive. The conversion of DP values to δ% (percentage of hydrolyzed glycosidic bonds) facilitates the true kinetic study of cellulose ageing.
- Colorimetry is a truly non-destructive method that facilitates the aesthetic aspect of the evaluation, but also provides clues concerning the chemical changes of the samples.
- FTIR spectroscopy is an ideal little-intervening method for the detection of lignin and kaolinite and the semi-quantitative determination of gelatine. The intensity of the 1720-35 cm^{-1} peak can be used for the monitoring of oxidation and for the evaluation of the effectiveness of washing and aqueous deacidification. All the above can be achieved non-destructively by the use of μ-FTIR.

Evaluation of the conservation treatments

The methods and the criteria discussed above were used for the evaluation of the conservation treatments applied in this work. Their application indicated that washing with deionized water is not an acceptable conservation treatment. Deacidification and consolidation were deemed adequate concerning the accomplishment of their goals, but with certain drawbacks. Deacidification resulted in chemical stabilization, but in many cases caused strength decrease. Consolidation with methylcellulose increased strength and had no negative effect on the rate of ageing, but did not offer any chemical stabilization. Simultaneous deacidification and consolidation in one step combined the positive effects of both treatments and lacked their defects, thus saving time and resources.

Proposed methodology and criteria for the evaluation

The following methodology is recommended as a loose protocol for the evaluation of paper conservation treatments:

- **General concept.** It is based on the determination of the short and long-term results of the intervention. The long-term results are studied on artificially aged samples. It also includes the comparison of the ageing rate of treated and untreated samples (see figure 1 and table 1).
- **Sample selection and preparation.** Four categories of samples (untreated, treated, untreated and aged, and treated and aged) must be prepared. The samples must consist of historical paper of about the same composition and age as the original paper that the treatment is to be applied. The use of more historical paper of various origins, compositions, and ages facilitates the expansion of the scope of the method application. It is also recommended that the method be tested on a standard paper of pure cellulose. The paper used for sample preparation should be blank, if possible unblemished, having no structural defects and watermarks and retain some strength. It is recommended that the paper leaves cut in strips suitable for the determination of the mechanical properties and in larger pieces for the colour determination. The test strips should be randomly assigned to the different sample categories and ageing intervals. This setup would hopefully result a more even sample distribution than the whole leaf assignment, alleviating errors caused by paper inhomogeneity. The samples should be stored in the darkness, preferably at standard conditions (23°C, 50%RH) and handled with clean latex gloves.
- **Methods for the determination of paper properties.** At least one mechanical, one colour, and one chemical property must be included in the evaluation scheme, since each category of properties registers changes that could be invisible to the others. From the mechanical properties, folding endurance is the most expedient. Tensile testing can detect the immediate impact of aqueous treatments and probably the effect of solvents other than water. The colour coordinate b* of the CIEL*a*b* colour system is recommended from the colour properties because it is more sensitive and related to the production of yellow chromophores.

Nevertheless, the choice of the colour property is not critical and the L* coordinate, which exhibits better repeatability but less sensitivity than b* or Brightness (B) can also serve the aesthetic evaluation. pH and DP are also recommended from the chemical properties, since pH is necessary for the evaluation of the effectiveness of deacidification and DP is a fundamental property, reflecting the condition of the cellulose macromolecules. In addition, both methods are sensitive and exhibit very good repeatability. FTIR spectroscopy can be used for paper characterization. Testing mechanical properties in both machine and cross direction is not necessary, since the results are the same. The direction that can produce more test strips should be chosen, depending on the paper leave dimensions. At least 10 measurements per sample are required for each mechanical property, but especially for folding endurance, it is recommended that all available paper be used, aiming to 40 or even 50 measurements per sample. Preconditioning and conditioning of the samples according to the appropriate standard is essential, especially before mechanical testing. If mechanical testing precedes the other tests, the paper used for it can be reused for the determination of DP and pH.

- **Accelerated ageing method.** Thermal ageing at high but not extreme temperatures (around 80°C) and RH (50-70%) should be implemented, according to the literature and the relevant standards. Better emulation of natural ageing is accomplished in sealed vessels[1, 6], and this is the main reason for recommending this ageing setup. The desirable RH inside the vessels can be adjusted either by preconditioning the samples at a suitable RH before sealing the vessels, or by the use of saturated solutions of appropriate chemicals. A preliminary ageing experiment will indicate the optimum ageing time interval or intervals, in the case of multi-interval ageing. It is preferable to apply ageing for several time intervals, so that graphs of the various paper properties versus time can be constructed. In the case that there is not enough paper, one ageing time interval is still sufficient for the evaluation. It is recommended that ageing should last long enough to produce considerable changes to paper properties, but without causing the collapse of the samples. In multi-interval ageing experiments, the longest interval should coincide with the breakdown of the samples (nullification of folding endurance).
- **Criteria justifying the conservation intervention.** Since every conservation intervention modifies the target object and may have harmful effects, it is justified only if it prolongs its useful life. This criterion is refined and adapted according to the treatment under study. Concerning the aqueous deacidification tested here, this criterion refinement specifies that *aqueous deacidification should apply to acidic paper and be followed by or better be combined with consolidation. It should be avoided in the case of neutral or alkaline paper, except if washing is required for aesthetic or other reasons.*
- **Criteria for declaring the intervention successful.** Three objective criteria originate from the three comparisons presented above (table 1), concerning the success of a conservation intervention:
  - The treatment should not bring about the immediate deterioration of the paper samples. The direct improvement of some paper properties is desired but rarely accomplished (immediate impact).
  - After accelerated ageing, the treated samples should exhibit better property values than the untreated ones (long-term effect).
  - The rate of ageing of the treated samples, determined by the rate of property deterioration, should be lower than that of the untreated (effect on the rate of ageing).

  All three criteria are rarely met for every property tested. In most cases, a ranking is inevitable, but no hard and fast rule can be proposed and the researcher has to decide on the basis of the available evidence. Usually, if criteria no 2 and 3 are met, a slight immediate deterioration of some paper properties is acceptable. The most compelling criterion seems to be no 2, but one should always consider if the chosen ageing period was adequate[11]. Nevertheless, a conservation treatment that does not meet all of the three criteria presented

above is imperfect. Thus, the endeavour to meet these criteria can result the improvement of the treatment. That is how an improved treatment came up, the simultaneous deacidification and consolidation, which combines the advantages and lacks the disadvantages of two imperfect treatments.

ACKNOWLEDGEMENTS

I would like to thank: Professor A. Moropoulou (National Technical University of Athens [NTUA], School of Chemical Engineering [SCE]), Dimitra Barba [NTUA] and Theodoros Pomonis, Christina Roidi, Fotini Mastroyiani and Maria Stasinopoulou (Paper and Textile Testing Department of the General State Chemistry Laboratory of Greece [GSCLG]). The experimental part of the research presented here took place at the Section of Materials Science and Engineering, SCE, NTUA and at the Paper and Textile Testing Department of the GSCLG.

ABSTRACT

In the second part of this article, the most important methods used for the determination of paper properties, which were produced by the literature survey and presented in the first part, were tested on various samples of paper and the results statistically elaborated. On the basis of these results, the most sensitive and repeatable methods were chosen and a loose experimental protocol for the evaluation of paper conservation interventions is proposed. The general concept of the evaluation is based on the determination of the short and long-term results of the intervention. The long-term results are studied on artificially aged samples. It also incorporates the comparison of the ageing rate of treated and untreated samples.

The following points concerning the proposed methodology are thoroughly discussed:

- Sample selection and preparation.
- Methods for the determination of paper properties.
  The following methods are recommended: folding endurance, the colour coordinate b* of the CIEL*a*b* colour system, pH, degree of polymerization and FTIR.
- Accelerated ageing method.
- Criteria justifying the conservation intervention.
- Criteria for declaring the intervention successful.

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