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1 **Title:** Decoupling hydrolysis and oxidation of cellulose in permanent paper aged under atmospheric conditions

2 **Authors:** Caroline Vibert^{a,b,c *}, Bruno Fayolle^a, Denise Ricard^b, Anne-Laurence Dupont^{c *}

3 ^aLaboratoire PIMM, Arts et Métiers Institute of Technology, CNRS, CNAM, HESAM Université, 151
4 boulevard de l'Hopital 75013 Paris (France)

5 ^bANDRA, French National Radioactive Waste Management Agency, F-92298 Châtenay-Malabry, France

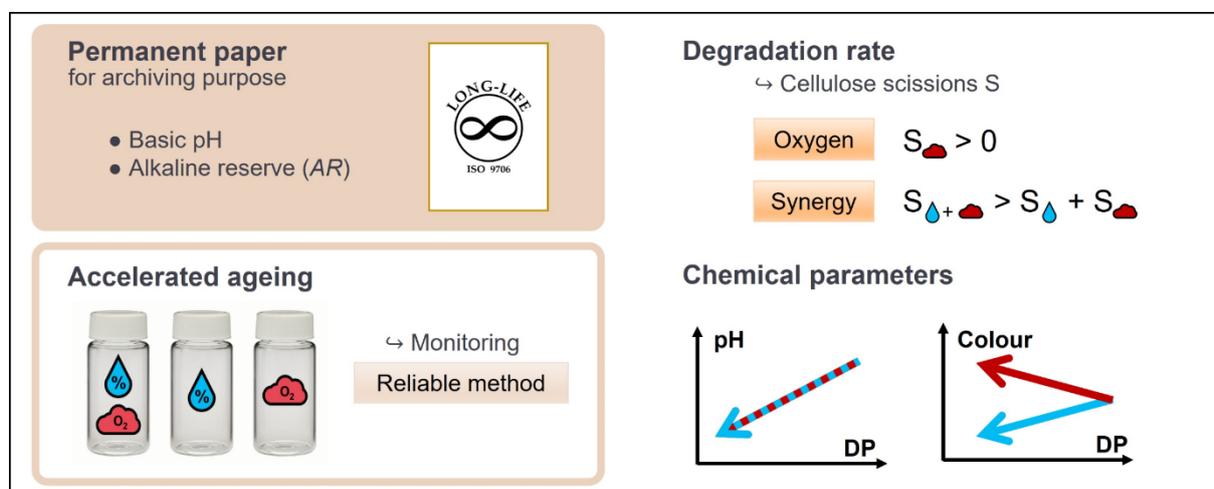
6 ^cCentre de Recherche sur la Conservation des Collections (CRC, CNRS UAR 3224), Muséum National
7 d'Histoire Naturelle, 36 rue Geoffroy St Hilaire 75005 Paris, France

8 *Corresponding authors: caroline.m.vibert@gmail.com; anne-laurence.dupont@mnhn.fr.

9 **Keywords:** Accelerated aging; Kinetics; Acidification; Alkaline reserve; Degree of polymerization; Coloration

10 **Abstract:** In order to investigate a synergetic role of water and oxygen in the degradation of permanent paper in
11 archiving climate, accelerated ageing in three different conditions was conducted: humid air, humid
12 nitrogen and dry air. This allowed to decouple acid-catalysed hydrolysis versus oxidation of cellulose.
13 After ensuring the reliability of the ageing experiment, the degradation state of the paper was assessed.
14 Various techniques (size exclusion chromatography, pH extraction, alkaline reserve, paper colour and
15 water content) were used. It appeared that the cellulose scission rate of the Canson® permanent paper
16 was reduced compared to the Whatman No. 40 acidic cotton paper used as reference, but not in the
17 same proportion for all the ageing conditions. This was attributed to a lower acidification, inhibiting
18 acid-catalysed hydrolysis, due to the presence of the alkaline reserve. The degradation mechanisms are
19 the same for both papers, which exhibited a similar chemical and physical degradation.

20



21 1. INTRODUCTION

22 Degradation of books and other paper documents is an essential issue in libraries and archives, especially with
23 acidic papers, some of whom present a catastrophic state in terms of mechanical behaviour. These institutions
24 follow climate guidelines for the conservation of their paper-based documents and can resort to treatments to
25 tackle both chemical and mechanical degradation. In particular, several deacidification treatments that leave an
26 alkaline reserve have been proven effective for hindering the decrease of pH of paper, a threatening issue for
27 paper degradation (Arney et al., 1980; Barrow & Sproull, 1959; Hubbe et al., 2017). In a review article, Baty
28 mentioned that these treatments are even more effective on least degraded papers (Baty et al., 2010). The use of
29 mechanically resistant alkaline paper in the first place is thus recommended to prevent cellulose degradation.
30 Such paper, known as permanent paper, is commercially available and is used in many applications for
31 conservation storage and for printing archival documents. However, its degradation in terms of mechanisms and
32 kinetics still needs to be understood and characterized, which is the aim of the present research.

33 The ISO 9706 standard for paper permanency was developed in the late 1990s to address the problem of the
34 long-term conservation of archival documents. It is based on four criteria that tackle both chemical and
35 mechanical degradation of the paper over time. The pH of the paper should lie between 7.5 and 10, its alkaline
36 content (called alkaline reserve) above 2 % in weight of calcium carbonate or equivalent, and its content in
37 oxidative compounds less than 1 %. The fourth criterion relates to mechanical strength and will not be discussed
38 here.

39 These criteria aim at avoiding paper acidification since acid-catalysed hydrolysis of cellulose is the main
40 degradation reaction that occurs during paper ageing under archival conservation conditions, *i.e.* at ambient
41 conditions of temperature, humidity, and pressure. The hydrolysis occurs at the glycosidic bonds in the cellulose
42 macromolecule and leads to random scissions. Under archival conditions, this reaction is mainly governed by
43 water and acidity of paper (Gehlen, 2010; Tétreault et al., 2019). The water content, which depends on the
44 relative humidity (*RH*) in the environment, acts as a solubilization medium for both acids and solid particles of
45 alkaline reserve (Emsley et al., 2000). The acids arise from the paper fabrication process and as by-products of
46 secondary reactions of the hydrolytic degradation. The criterium of pH basicity aims to tackle the former, and the
47 alkaline reserve the latter. In permanent paper, calcium carbonate is the most common alkaline reserve.

48 The efficiency of the alkaline reserve deposited through deacidification treatments in old books and acidic papers
49 has been proved, and the amount of calcium carbonate has been related to a reduction of the hydrolysis rate (Ahn

50 et al., 2012, 2013; Horst et al., 2020; Malesic et al., 2002). However, whether a modern permanent paper
51 behaves similarly as a naturally aged and deacidified paper is still unknown. Is the degradation halted until the
52 alkaline reserve is consumed or does the acidification continue at a slow pace? This is one of the questions
53 addressed in this research.

54 To this purpose, all the degradation pathways need to be examined. In particular, besides acid-catalysed
55 hydrolysis, cellulose is also prone to oxidation by the oxygen in air due to its high content in hydroxyl groups
56 (Kolar, 1997). Oxidative degradation of cellulose has been studied by many authors and several mechanisms
57 have been proposed. Oxidation is responsible for the introduction of carbonyl and carboxyl on the glucose ring
58 (Margutti et al., 2001; Potthast et al., 2005). At alkaline pH, oxidized cellulose can undergo β -alkoxy elimination
59 reactions, which lead to chain cleavage. If these reactions have been shown to happen in oxidized model pulps
60 during an alkalinisation treatment, they have barely been found in naturally oxidized papers (Ahn et al., 2012;
61 Glaus & Van Loon, 2008; Hosoya et al., 2018). On the other hand, it has been shown that random cellulose
62 cleavage was also enhanced at acidic pH in chemically oxidized pulps. The most agreed upon explanation is that
63 oxidized moieties, and essentially carbonyls, could modify the reactivity of the glycosidic linkage towards
64 hydrolysis. The so-called weak-bonds (glycosidic bonds with neighbouring oxidized groups) lead to a higher
65 hydrolysis rate (Rånby, 1961). Lastly, by combining wet conditions with oxygen, a synergetic effect has been
66 shown (Emsley et al., 2000). While this phenomenon was proven under highly oxidative artificial ageing
67 conditions, there is to our knowledge little evidence of that happening in archival conditions. Zou reported that
68 the degradation of an acidic cotton paper was similar under nitrogen atmosphere and in air at 40 % RH (Zou et
69 al., 1994). However, the hypothesis that because a reduction in the hydrolytic reaction rate in the case of alkaline
70 papers, the oxidative environment may take a more prominent role and become a key factor in the degradation
71 cannot be ruled out.

72 Taking all these factors into consideration, the aim of this research was to study the degradation pathways of
73 permanent paper in archival conditions compared to acidic paper. We addressed the question by taking into
74 account the two main degradation mechanisms: acid-catalysed hydrolysis and oxidation, and by decoupling them
75 to identify their respective roles. Hydrolysis was studied using various RH, and oxidation through the presence
76 or absence of oxygen as ageing parameters. Light, pollutants, and biochemical reactions were not considered, as
77 climate-controlled storage rooms are dark and often ventilated.

78 In order to reach various degraded states, accelerated ageing was used. It consists in reproducing the reactions
79 that occur in ambient conditions in archival storage rooms, but at higher temperatures, and often, higher
80 humidity. Among the proposed methods, studies usually mention temperatures from 50 to 100 °C to avoid
81 thermal degradation or high temperature alkaline scissions (Brillard et al., 2017; Knill & Kennedy, 2003).
82 Relative humidity conditions can also be controlled, 50 % *RH* reproduces the conditions of an archive storage
83 room. Paper degradation produces volatile acids that can auto-catalyse cellulose hydrolysis, as shown by the
84 large differences in the degradation of a confined versus a free-surface paper in a stack (Carter et al., 2000). The
85 use of closed vessel or vials allows to better reproduce this phenomenon (Bégin & Kaminska, 2002). This being
86 the most suitable accelerated ageing method for paper, it was chosen for this study. However, tightening of the
87 tubes must be adequate because leakage of humidity can occur. Some authors propose to monitor the weight of
88 the tubes during the ageing to evaluate the possible flows of humidity and to correct the actual hygrothermal
89 conditions with time (Jeong & Potthast, 2021; Sawoszczuk et al., 2008). Here, to ensure trustworthy
90 experimental results, we evaluated the robustness and reliability of the accelerated ageing technique in closed
91 tubes beforehand.

92 Paper degradation can be assessed using different parameters, either chemical, mechanical, or physical. Among
93 these, the decrease in the average length of the cellulose macromolecules and hence in its degree of
94 polymerisation (*DP*) is the most representative. It is used to define the number of scissions per glucose monomer
95 *S* (Calvini, 2012; Ding & Wang, 2008; Ekenstam, 1936):

$$96 \quad S = 1/DP - A/DP_0 \quad (1)$$

97 The *DP* was thus the main parameter used in this study. Other chemical and physical measurements at the paper
98 macroscopic level were also used. These include pH, alkaline reserve, and colour. The pH and alkaline reserve
99 gave information about the acids production (Ahn et al., 2013; Carter et al., 2000; Horst et al., 2020).
100 Equilibrium moisture content (*EMC*) was taken into consideration as an indirect measure of the crystallinity and
101 polarity of the cellulose and the paper porosity (Driemeier et al., 2012; Kerekes & McDonald, 2020). Lastly,
102 colour measurement provided evidence of the chromophores production and is particularly relevant in the case of
103 lignin containing papers. This measurement is moreover widely used for paper conservation assessment (Ahn et
104 al., 2019; Rosenau et al., 2017; Zervos & Moropoulou, 2005; Zou et al., 1993).

105 In the following, the reliability of the accelerated ageing method will first be evaluated. The state of degradation
 106 of the two papers in different accelerated ageing conditions will be assessed, then the chemical consequences
 107 will be analysed and interpreted.

108

109 2. MATERIALS AND METHODS

110 2.1. Paper samples

111 Two papers were selected for this study: a permanent paper and a cotton paper as control. The permanent paper
 112 is a bleached kraft pulp paper from Canson® (Canson® barrier paper) made with a mix of hardwood and
 113 softwood fibres. Its pH, alkaline reserve (*AR*) and Kappa number comply with the ISO 9706 standard for paper
 114 permanency. Filter paper Whatman No. 40 made of cotton linters was used as acidic paper reference and it is
 115 referred hereafter as Whatman paper. It is exclusively composed of cellulose. This paper has been widely tested
 116 in the literature and can easily serve for comparisons. The main characteristics of the two papers are specified in

117 **Table 1.** Properties of the two selected papers at initial state: nature of the fibres, grammage, pH, alkaline reserve (*AR*), Kappa index,
 118 equilibrium moisture content (*EMC*) at 23 °C and 50 % *RH*, and thickness.

Paper	Fibres	Grammage (g·m ⁻²)	pH	<i>AR</i> (%)	Kappa number	<i>EMC</i> (%)	Thickness (µm)
Whatman	cotton	95	5.7 ± 0.2	/	/	4.9 ± 0.1	210 ± 10
permanent	wood	80	8.9 ± 0.2	3.3 ± 0.3	2.6	6.2 ± 0.1	100 ± 10

119

120 2.2. Accelerated ageing

121 Accelerated ageing experiments were conducted at 90 °C under three different atmospheres: humid air, humid
 122 nitrogen, and dry air. Relative humidity (*RH*) for humid conditions was set to 50 %, as recommended for
 123 archival paper storage and accelerated ageing (TAPPI T544 sp).

124 Samples were aged in 15 cL Wheaton® glass tubes. 4.00 ± 0.01 g equivalent of dry paper cut in strips
 125 (1.5 × 12 cm) was introduced in each tube, *i.e.* 4.28 g of permanent paper or 4.22 g of Whatman paper. The tubes
 126 were closed with a polypropylene screw cap and a PTFE septum (Duran Groups®, max. 140 °C). A three-
 127 layered gas impermeable film (IN SITU Museum & Archive Services®, PET, aluminium and polyethylene) was
 128 added between the tube and the septum.

129 The tubes were preconditioned opened at 23 °C at the given *RH* and gas atmosphere as reported in **Table 2**, then
 130 closed directly in the conditioning atmosphere. Humid air tubes were preconditioned at 50 % *RH* and 23.0 °C for
 131 48 h in a climatic room (CTS®) with controlled humidity and temperature. Humid nitrogen tubes were stored for

132 48 h in a glove box (Jacomex®) with controlled humidity, temperature, and partial pressure in oxygen. The
 133 glovebox instrument indicated 48 % *RH* and 0.0 ppm of oxygen partial pressure at 23.0 °C. Dry air tubes were
 134 dried in an oven at 105 °C for 2 h, as recommended in TAPPI T 573 pm. The humidity inside the tubes after
 135 closure was 10 % as measured by hygro-buttons.

136 After closure, the tubes were placed at 90 °C. Humid air and humid nitrogen tubes were aged in a climatic
 137 chamber set at 50 % *RH* (Weiss® WK3) and dry air tubes in an oven (Air Performance® AP60). Fixing the
 138 same *RH* in and out the tubes prevented water vapour flows. The tubes were kept in the dark during the whole
 139 ageing period. They were removed after 2, 4 and 10 weeks. After ageing, the paper was kept in a climatic room
 140 at 23 °C and 50 % *RH* until testing. Two replicate tubes were prepared for each paper, condition, and ageing
 141 time. The diffusion of oxygen or nitrogen in paper was considered negligible due to the low thickness and
 142 density, as indicated by the low grammage. The degradation was therefore considered homogenous through the
 143 paper sheets.

144 A validation method was developed to assess eventual water vapour leakage during the ageing. Two tubes were
 145 filled with 4.22 g of Whatman paper, preconditioned for 48 h at 50 % *RH* and 23 °C in air in the controlled
 146 climate room and the ageing was conducted at 70 °C in an oven (Mettmert® UN55). Hygrobuttons from
 147 Plug&Track® (accuracy of 0.1 °C and 0.5 % *RH*, 1 measure per hour) were placed in the tubes to record
 148 temperature and humidity during the ageing period. The temperature of 70 °C is below the working limits of the
 149 hygrobuttons. An oven (the *RH* in the oven at 70 °C is 3 %) was chosen over a climate chamber (humid
 150 atmosphere) to emphasize the *RH* gap between inside and outside the tubes.

151 **Table 2.** Conditioning and ageing method in the tested conditions.

Conditions	Preconditioning at 23 °C	Target <i>RH</i> at 23 °C	Measured <i>RH</i> at 23 °C	Ageing at 90 °C
Humid air	Climatic room (48 h)	50 %	50 %	Climatic chamber at 50 % <i>RH</i>
Humid nitrogen	Glove box (48 h)	50 %	48 %	Climatic chamber at 50 % <i>RH</i>
Dry air	Oven at 105 °C (2 h)	0 %	10 %	Oven
Control	Climatic room (48 h)	50 %	50 %	Oven

152

153 2.3. Analytical characterization

154 The degree of polymerisation (*DP*) was measured by size-exclusion chromatography (*SEC*). The samples were
 155 prepared according to Dupont (Dupont, 2003). Paper (10.40 mg) was ground in water, followed by solvent
 156 exchange in methanol, then in DMAc (*N,N*-dimethylacetamide). It was dissolved in DMAc/LiCl (8 % w/v) and
 157 diluted 16 times in DMAc to the approximate concentration of 0.625 mg·mL⁻¹. Before the analysis, the samples
 158 were filtered on a 0.45 µm pore PTFE membrane. The following set-up was used: isocratic HPLC pump (515,

159 Waters®), autosampler (UltiMate 3000, Dionex), MALS detector (Wyatt Technologies® Dawn EOS, 60 °C) and
160 differential reflective index detector (Waters® 2414, 55 °C). Each sample was run three times on 4 PLGel
161 miniMIX A columns (Agilent®, 20 µm, 4.6 × 250 mm, 60 °C). The injected volume was 100 µL and the flow
162 rate 0.4 mL·min⁻¹. The chromatograms are analysed with Astra® software (Astra® 5.3.4.14, Wyatt
163 Technologies®). The bimodal molar mass distribution graphs were analysed by manually separating at the valley
164 between the two peaks, as proposed by Dupont (Dupont et al., 2018).

165 Chemical parameters were obtained using standard TAPPI methods. The cold extraction pH of paper was
166 measured according to TAPPI method T 509 om. 100 mg of paper was used instead of 1 g because of the low
167 quantity of available paper, and the volume of water was adjusted proportionally. Alkaline reserve (AR) was
168 evaluated according to TAPPI method T 553 om. The results are expressed in calcium carbonate equivalent.
169 Similarly as for pH, 100 mg of paper was used. Kappa number was measured according to TAPPI method
170 T 236 om with 1.3 g of paper. At least 3 replicas were prepared for each sample. All reactants used for DP, pH,
171 AR and Kappa number determination were of analytical grade.

172 EMC was measured by dynamic vapour sorption (DVS). Isotherms at 30 °C in the range from 0 % to 90 % RH
173 were carried out on the samples (5 to 10 mg). For practical reasons, two Surface Measurement Systems® DVS
174 instruments were used: a DVS Advantage for the measurements on Whatman paper and a DVS-1000 for
175 permanent paper. Control unaged papers were tested on each machine.

176 The coloration of paper was measured in $L^*a^*b^*$ CIE 1976 colour space with a spectrophotometer (Konica
177 Minolta® CM-26d) coupled with the SpectraMagic NX software, using 8 mm diameter aperture, specular
178 component included (SCI, 10° angle). L^* coordinate varies from black to white, a^* from green to red and b^*
179 from blue to yellow. Six paper strips from each ageing tube were used for a total of 10 measurements. Thickness
180 was measured with a digital micrometer (Mitutoyo® Digimatic) on several paper sheets and the mean value is
181 reported.

182 **3. RESULTS AND DISCUSSION**

183 **3.1. Validation of the accelerated ageing method**

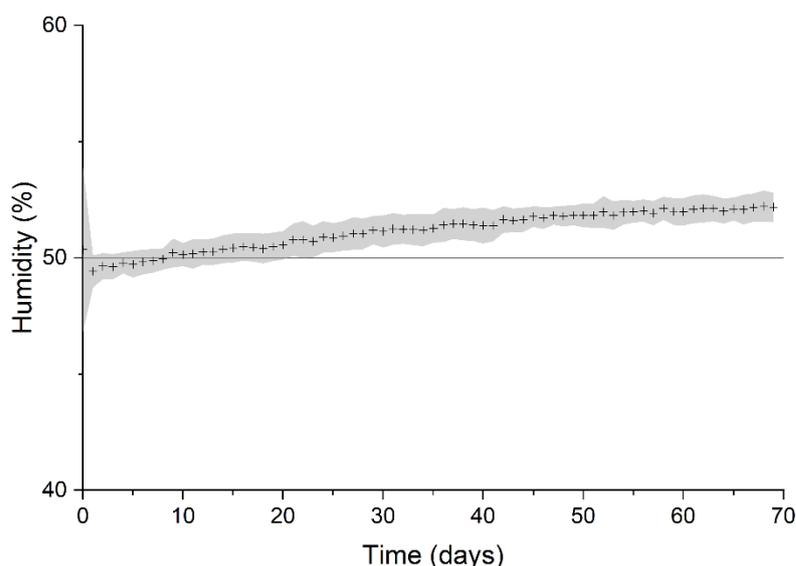
184 The experimental work was based on the accelerated ageing of two different types of paper under three ageing
185 conditions to discriminate the role of water and oxygen on the degradation of permanent and acidic paper. To
186 ensure the reliability of the results, the accelerated ageing method was tested through the monitoring of water

187 vapour in control tubes. The reproducibility of the method was evaluated using a deviation index to quantify the
188 differences between two tubes aged in the same conditions.

189 3.1.1. Monitoring of the relative humidity inside the tubes

190 No leaks of water were measured during the 10-week ageing of the control tubes. **Figure 1** shows the evolution
191 of the *RH* inside the control tubes filled with Whatman paper and aged at 70 °C. Unexpectedly, humidity
192 increased from 49 % to 52 % in 10 weeks. This difference is significant regarding the fact that 4 hygro buttons,
193 two in two tubes, recorded the same variation with an accuracy of 0.5 % *RH*.

194



195

196 **Figure 1.** Evolution of the relative humidity inside closed tubes aged in an oven at 70 °C for 70 days in presence of 4 g of Whatman paper,
197 standard deviation in grey.

198 The small increase in *RH* observed over 70 days in **Figure 1** was investigated. Three phenomena were examined
199 in relation to this observation. Firstly, the hydrolysis of amorphous cellulose releases water as amorphous zones
200 account for water adsorption sites (Jeong & Potthast, 2021; Tétreault et al., 2019). In contrast, this reaction
201 consumes a water molecule per bond scission. Thirdly, water vapour leakage could eventually happen through
202 the cap of the tubes. All the following calculations are described in the **Appendix. A**. On the one hand, the raise
203 from 49 to 52 % *RH* corresponds to an increase of $n_{RH} = 0.05 \pm 0.01$ mmol of water per tube. On the other hand,
204 the first hypothesis, *i.e.*, the release of water from cellulose degradation, was estimated as $n_{EMC} = 0.4 \pm 0.2$ mmol
205 of water per tube from DVS measurements at 70 °C and 50 % *RH*, in sorption regime. The second hypothesis

206 accounts for water consumption through hydrolysis. As the DP_n of Whatman paper dropped from 360 to 310,
207 this corresponds to $n_s = 0.01$ mmol of water consumed during the ageing. In total, the balance of flows can be
208 evaluated as the difference between the released and consumed water. Considering the standard deviation, no
209 more than $n_{\text{flows}} = 0.6$ mmol of water might have possibly leaked outside the tubes in 70 days. Since about
210 8 mmol of water are contained in a tube during ageing, leaks seem negligible.

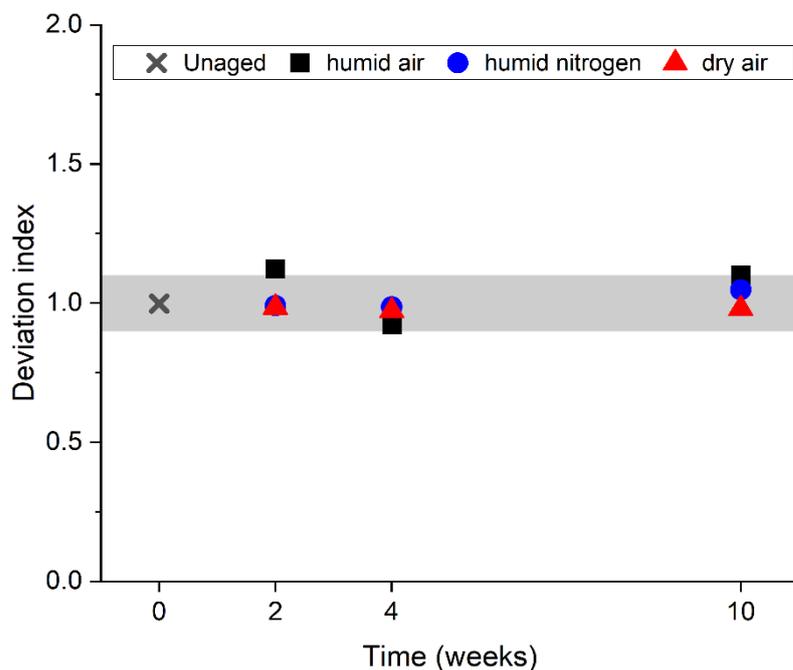
211 Interestingly, other authors showed an important drop of RH during ageing in closed vials at similar temperature,
212 with a decrease of 30 % in 80 days at 65 °C (Jeong & Potthast, 2021). They linked this decrease with the
213 presence of water vapour flows outside the closed vials and, as the concentration in water influences the
214 hydrolysis rate, they proposed a recalculation method to account for the loss of water. Their result can be
215 explained by the fact that they used only 400 mg of paper in a similar tube volume, thus limiting the production
216 of water due to change in EMC . The tightening of the tubes and the absence of impermeable film could also be
217 called into question. In the present work, it will not be useful to take into account an evolution of RH in the tubes
218 as part of the degradation process.

219 3.1.2. Reproducibility of the ageing method

220 To control the reproducibility of the ageing, a deviation index is introduced. It quantifies the differences between
221 the two replicate tubes prepared for each paper, condition, and time. This deviation index (DI) is based on the
222 colour coordinate b^* . The detail of the calculation is explained in the **Appendix. B**. The coordinate b^* was
223 chosen because it is highly sensitive to small changes and its measurement is reproducible and easy to perform.
224 The closer the deviation index to 1, the less likely errors in the ageing method.

225 DI is plotted **Figure 2** for each condition and duration. DI was close to 1 in all cases, showing that there was no
226 significant difference between two replicate tubes aged in the same conditions. The index did not increase with
227 ageing time either, as it would have in the presence of flows. This is another evidence of the absence of

228 significant leakage from or into the tube.



229

230 **Figure 2.** Deviation index (inter over intra-tubes standard deviation ratio) calculated from the b^* coordinate measurements. Grey zone
231 corresponds to $DI = 1 \pm 10\%$.

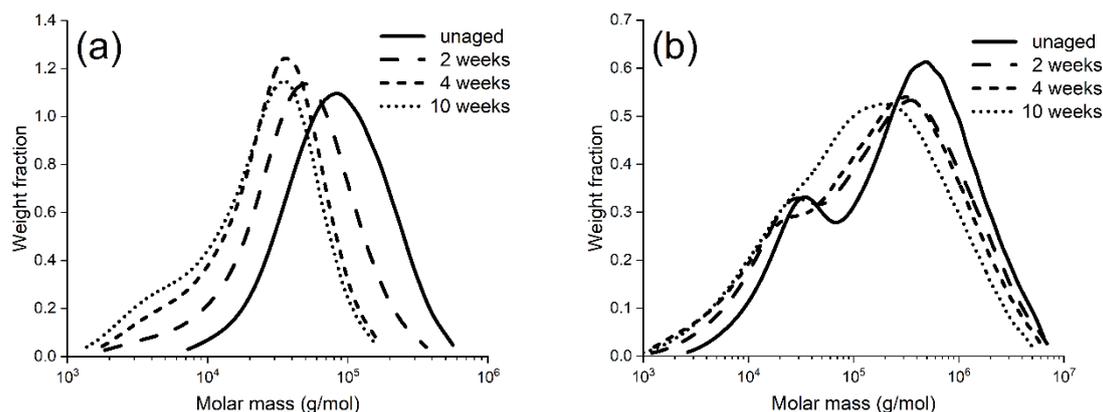
232 All in all, the accelerated ageing method used in this study was robust and reproducible, as no flow was
233 evidenced in 10 weeks. Water was the only assessed parameter for flows evaluation, but it can be assumed that
234 neither oxygen, nitrogen nor volatile acid compounds could flow during the ageing thanks to the multi-layered
235 barrier film added between the tube and the septum (§2.2.). Additionally, the use of two ageing tubes for each
236 paper, condition and time insures the reliability of the results.

237 3.2. Macromolecular changes

238 As reported in the introduction, the degradation of paper can be directly related to the scissions of the cellulose
239 chains, measured with the degree of polymerisation (DP) as analysed by *SEC*. This enables the comparison of
240 the hydrolysis reaction rates between the different conditions.

241 Molar Mass Distribution (*MMD*) of cellulose for the samples aged under humid air is shown **Figure 3**. For
242 unaged Whatman paper, the distribution is monomodal with one unique peak that corresponds to cellulose
243 molecules size distribution. The *MMD* evolved to lower molar masses with ageing and the peaks became sharper
244 ($M_w = 110,000$, $DP_w = 700$, $DP_n = 360$ to $M_w = 34,000$, $DP_w = 210$, $DP_n = 90$). This indicates cellulose scissions

245 at random positions in the chain, as reported in the literature (Dupont et al., 2018; Nevell & Zeronian, 1985;
 246 Stephens et al., 2008). The dispersity increased from 2.0 to 2.4 in 10 weeks, which is consistent with a shoulder
 247 appearing at low molar masses side already after 4 weeks. Stephens et al. had the same observation and
 248 attributed it to the progressive appearance of small cellulose chains (Stephens et al., 2008). The molar mass of
 249 the shoulder being centred below 50, it is consistent with cellulose oligomers.



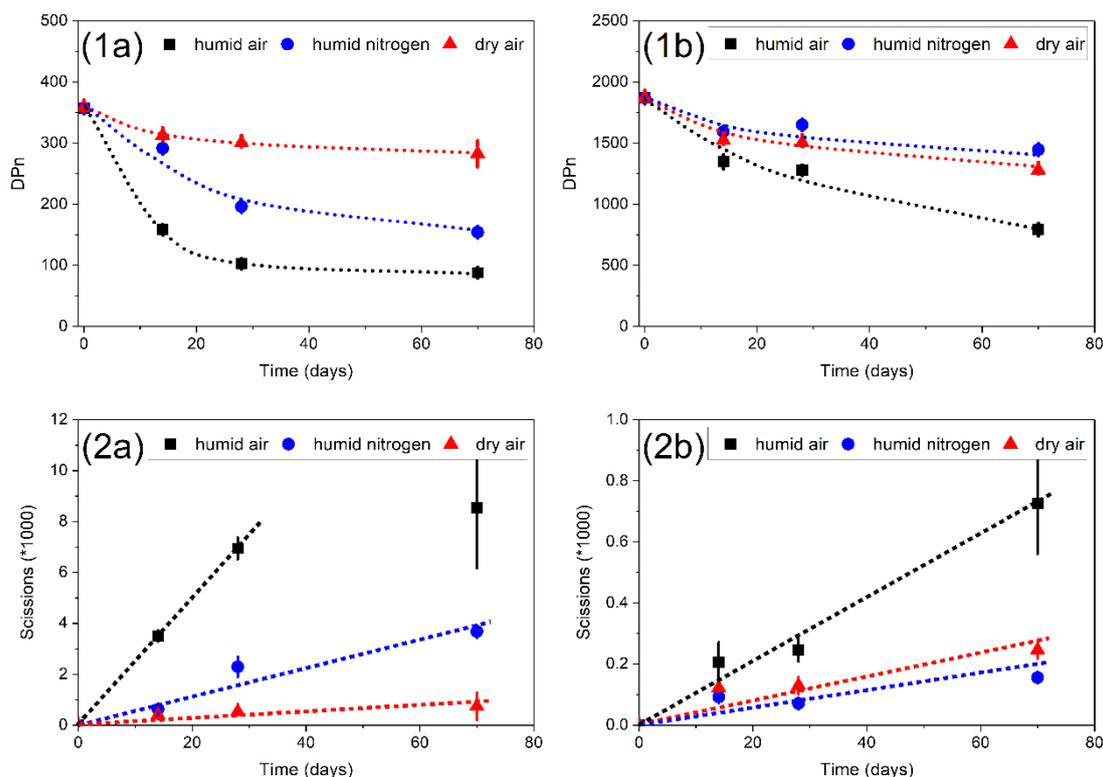
250
 251 **Figure 3.** Molar mass distribution for the Whatman paper (a) and permanent paper (b) aged under humid air condition for different ageing
 252 times.

253 The *MMD* for permanent paper exhibited a bimodal distribution (**Figure 3b**): indeed, wood fibres contain
 254 hemicelluloses of lower molar masses that are not present in cotton fibres (Knill & Kennedy, 2003). As for
 255 Whatman paper, the cellulose peak shifted to low molar masses with ageing ($M_w = 890,000$, $DP_w = 5500$,
 256 $DP_n = 1870$ to $M_w = 460,000$, $DP_w = 2800$, $DP_n = 360$), similarly to literature data for wood pulp paper cellulose
 257 (Dupont et al., 2018; Hill et al., 1995). The peak also widened as the paper aged, with a dispersity increasing
 258 from 2.9 to 3.6 due to the formation of shorter cellulose chains and the progressive merger of cellulose and
 259 hemicelluloses peaks. The tendency was similar for all the ageing conditions.

260 The DP_n of cellulose as a function of time is plotted for both papers **Figure 4 (1)**. The shape of all six curves is
 261 similar and shows a maximal decrease rate at the beginning of the ageing, followed by a deceleration for longer
 262 exposure times. This shape is characteristic for cellulose ageing (Tétreault et al., 2019; Zou et al., 1994). In
 263 humid air conditions, DP_n decreased by 60 % for Whatman paper and by 30 % for permanent paper. For both
 264 papers, the 10-week ageing is sufficient to reach a significant degradation state, allowing further comparisons of
 265 the DP_n evolution.

266 Moreover, it can be noticed that the DP_n of Whatman paper under humid air remained constant between 4 and 10
 267 weeks, at a plateau value of 90. It corresponds to the levelling-off degree of polymerisation ($LODP$), defined as
 268 the asymptotic value indicating that the amorphous zones have been significantly hydrolysed (Battista et al.,
 269 1956). The $LODP$ value is usually found around 100 to 150 depending on the fibres, which is consistent with our
 270 value (Calvini, 2005). The plateau was not reached for other ageing conditions nor for permanent paper.

271 **Figure 4 (2)** shows that the evolution of the number of cellulose scissions with time, calculated according to **Eq.**
 272 **1**, was almost linear provided that the last data point for Whatman paper in humid air ageing is not taken into
 273 account since $LODP$ is reached. The constant rate of cellulose scissions is consistent with a degradation reaction
 274 at order 1 according to Ekenstam equation (Ekenstam, 1936). No acceleration of the degradation for longer
 275 ageing time was observed, as expected in closed tubes where auto-catalysis is supposed to take place (Calvini et
 276 al., 2008; Emsley et al., 2000; Hill et al., 1995; Poggi et al., 2014). As a result, it is possible to compare the
 277 ageing conditions through the scission rates.



278

279 **Figure 4.** Effect of ageing conditions on the depolymerisation of cellulose expressed in terms of DP_n (1) and of number of scissions (S) per
 280 glucose unit (2) for Whatman paper (a) and permanent paper (b)

281 The degradation rates (k) are given in **Table 3**. As expected, permanent paper degraded more slowly than
 282 Whatman paper. The rates for Whatman paper were close to the values found in the literature. For example, for
 283 the same Whatman No. 40, Zou found 82×10^6 scissions per day under air at 40 % *RH*, 52×10^6 under nitrogen
 284 at 40 % *RH* and 18×10^6 under dry air (Zou et al., 1994). Although the ageing conditions were not identical, the
 285 rates are in the same order of magnitude. Moreover, the rates found for the ageing at 50 % *RH* are higher than
 286 those at 40 % *RH*, which agrees with a water-controlled acid-catalysed hydrolysis degradation model. The
 287 predominance of humid nitrogen over dry air in the case of Whatman paper was also observed in other studies,
 288 for example for kraft paper aged in oil at 140 °C, where the amount of water plays an extended role compared to
 289 the amount of oxygen (Emsley et al., 2000). However, for permanent paper the rates for humid nitrogen and dry
 290 air were similar. Permanent paper is thus more sensitive to oxygen degradation than Whatman paper.

291 All the degradation rates were lower for permanent paper than for Whatman paper. However, with the rate being
 292 25 times lower in humid air and 23 times lower in humid nitrogen conditions, dry air condition is the least
 293 slowed down, being reduced by a factor of only 3. The strong reduction in humid conditions means that
 294 permanent paper is less sensitive to humidity-driven reactions than Whatman paper. This can be attributed to a
 295 smaller hydrolysis catalysis, due to the difference in initial acidity of the papers (Bégin et al., 1998) and to the
 296 presence of the alkaline reserve in permanent paper. As a result, the ratio between the rate in humid nitrogen and
 297 dry air shifts from 5 for Whatman paper to 1 for permanent paper. Water and oxygen have similar impact on its
 298 degradation.

299 Moreover, the results also show that the degradation in humid air is enhanced compared to the sum of dry air and
 300 humid nitrogen conditions, the rate for humid air being higher by 60 % for permanent paper and by 270 % for
 301 Whatman paper than the cumulated rates in dry air and humid nitrogen. This leads to consider a synergetic
 302 process driven by water and oxygen in the degradation of the two papers. Although it has been demonstrated
 303 earlier and only in the case of chemical oxidation (Wilson & Parks, 1979), the synergy between hydrolysis and
 304 oxidation by the oxygen in the air is clearly evidenced here for the two papers.

305 **Table 3.** Degradation rate constants k at 90 °C expressed as a number of scissions per glucose unit per day, equilibrium moisture content
 306 (*EMC*) measured at 30 °C, pH and alkaline reserve (*AR*) for initial state and after 10-week ageing.

Paper	Ageing conditions	k ($\times 10^6 \text{ day}^{-1}$)	<i>EMC</i> at 30 °C (%)	pH	<i>AR</i> (%)
Whatman	<i>unaged</i>	/	4.9	5.7	/
	humid air	250 ± 1.4	3.5	4.4	/
	humid nitrogen	56 ± 11.8	4.0	5.3	/
	dry air	12 ± 4.8	4.4	5.3	/
permanent	<i>unaged</i>	/	6.2	8.9	3.3
	humid air	10 ± 1.2	5.6	8.5	2.9
	humid nitrogen	2.4 ± 1.0	5.8	8.8	3.1
	dry air	3.8 ± 1.2	6.0	8.8	3.2

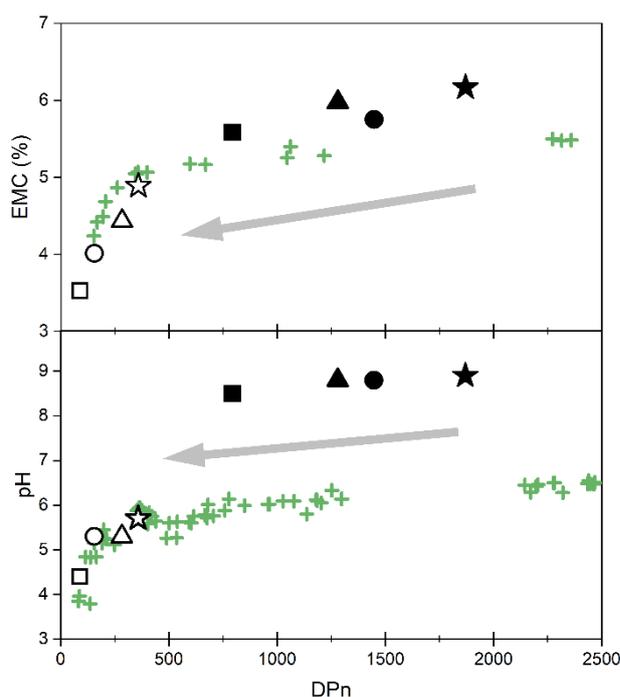
307

308 **3.3. Macroscopic changes**

309 The water and acids content are essential parameters in the degradation reactions, as well as the quantity of
 310 alkaline reserve in neutralizing the acids in the case of permanent paper. The coloration of paper was also
 311 monitored, as a clue for chromophores production, in relation with the degradation.

312 **3.3.1. Water content**

313 The equilibrium moisture content (*EMC*) of papers at initial and final ageing stages are presented **Table 3**. For
 314 both papers, *EMC* decreased with time in all ageing conditions: humid air caused the fastest decrease, and dry air
 315 the slowest. Moreover, the decrease in 10 weeks under humid air was more important for Whatman paper: by
 316 30 % of the initial value versus 10 % for permanent paper.



317

318 **Figure 5.** Equilibrium moisture content (measured at 30 °C for 50 % *RH*) and pH of paper as a function of DP_n (initial values ★, humid air
 319 ■, humid nitrogen ●, dry air ▲; empty symbols for Whatman paper and full symbols for permanent paper). Literature data for acidic and
 320 neutral cotton paper are superimposed (in green crosses, data from [Tétreault et al., 2019]). The progress of ageing is indicated by the arrows.

321 Given these observations, we investigated the relation between water content and degradation (**Figure 5**). In a
 322 first approximation, a linear correlation between *EMC* and DP_n appears independently of the ageing conditions.
 323 The observed decrease of *EMC* can be attributed to the progressive degradation of the amorphous zones of the

324 cellulose, due to the scissions preferentially occurring in these areas (Gehlen, 2010). The data of Tétreault et al.
325 for neutral and acidic cotton papers (same as Whatman paper used here) aged at 100 °C in humid air (Tétreault et
326 al., 2019) are displayed on the same graph. Our data followed the same trend showing a higher slope at lower
327 molar masses. The evolution of *EMC* indicates that the degradation mechanisms are similar for both papers and
328 therefore that only the kinetics are different.

329 3.3.2. Acidification

330 The degradation of cellulose is accompanied by an acidification of the paper via the production of acid
331 compounds as degradation by-products (Dupont et al., 2007; Glaus et al., 1999; Lundgaard et al., 2005). A
332 decrease in pH was observed with a difference of 0.4 units for the permanent paper and 1.3 units for the
333 Whatman paper in 10 weeks under humid air conditions (**Table 3**). This variation is significant since the latter
334 value corresponds to one order of magnitude in terms of hydronium concentration.

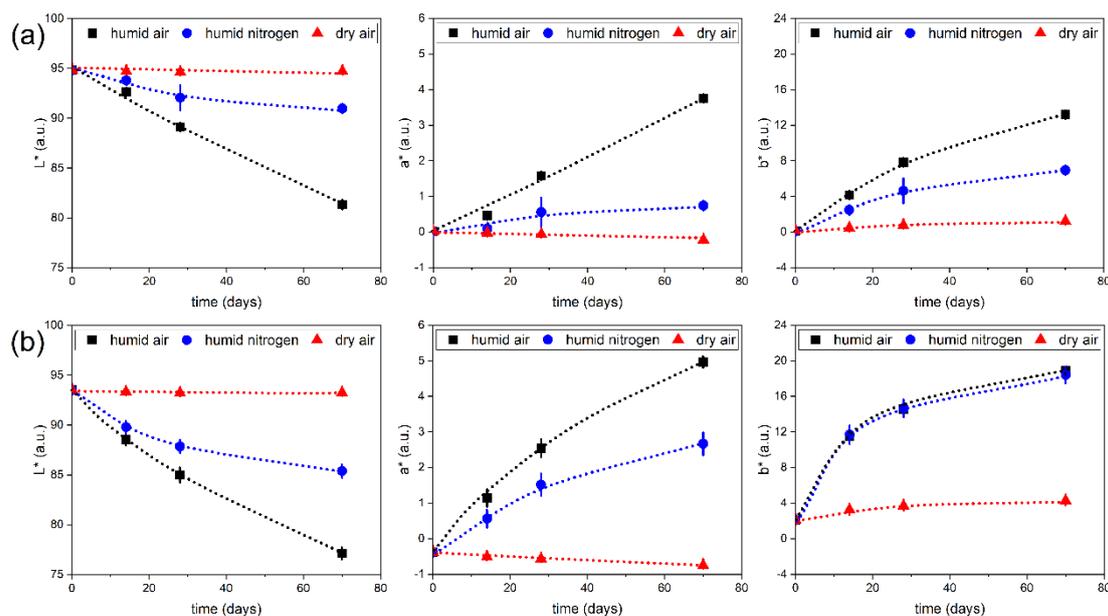
335 The acidification is linear with the decrease in DP_n for each paper, depending only slightly on the degradation
336 conditions (**Figure 5**). For Whatman paper, the values superimposed well with Tétreault's data, and other studies
337 on the same paper have also shown similar acidification (Tétreault et al., 2019; Zervos & Moropoulou, 2005).
338 For the permanent paper, as expected, acidification is slower, as shown by the lower slope.

339 The presence of alkaline reserve (*AR*) in permanent paper is supposed to neutralize the acids formed during the
340 degradation (Ahn et al., 2013; Bégin et al., 1998; Poggi et al., 2014). For this reason, the *AR* of permanent paper
341 after ageing was investigated (**Table 3**). No consumption of the *AR* was detectable. This might be explained by a
342 large excess of alkaline content, overriding its consumption. This hypothesis was tested by calculating the
343 production of acids and comparing to the alkaline reserve. Let us consider the number of acids formed per
344 cellulose scission in Whatman paper as reference. Under the 10-week humid air ageing, around $4 \times 10^{-5} \text{ mol} \cdot \text{g}^{-1}$
345 of hydroniums and $5 \times 10^{-5} \text{ mol} \cdot \text{g}^{-1}$ of cellulose scissions were produced, giving the ratio of one acid per
346 scission. Considering permanent paper, the number of scissions under the same conditions is $4 \times 10^{-6} \text{ mol} \cdot \text{g}^{-1}$,
347 assuming that cellulose and hemicelluloses have a similar hydrolysis rate and represent the whole dry mass
348 (Mäki-Arvela et al., 2011). According to the acids production ratio determined for Whatman paper, it is
349 equivalent to $4 \times 10^{-6} \text{ mol} \cdot \text{g}^{-1}$ of hydroniums formed in the permanent paper. Knowing that the amount of *AR* is
350 3.3 %, i.e., $7 \times 10^{-4} \text{ mol} \cdot \text{g}^{-1}$, one can conclude that the alkaline reserve is largely in excess compared to the acids
351 formation.

352 However, the results showed that the acidification of permanent paper was not totally stopped despite the
353 presence of AR. Some studies show no acidification of paper in presence of an alkaline content, but others
354 indicate a continued acidification in paper treated with deacidification methods. For example, Horst showed a
355 decrease of the pH from 10 to 7 during 50 years of natural ageing, whereas some AR still remained (Horst et al.,
356 2020). Moreover, several studies point out the question of diffusion and reactivity of AR since the particles are
357 heterogeneously distributed in the paper (Bégin et al., 1998; Hubbe et al., 2017). As a result, they could diffuse
358 and react slower than the production of acids. All these reasons could explain an acidification without
359 modification of the alkaline content.

360 **3.3.3. Coloration**

361 The coloration of paper with ageing was investigated measuring the $L^*a^*b^*$ coordinates (**Figure 6**). A global
362 trend to darkening (L^*) and yellowing (b^*) was evidenced. The shapes of the slopes are similar between the two
363 papers indicating analogous behaviour. In particular, the yellowing decelerates for extended ageing. This is
364 consistent with the data of Bülow for acidic paper aged in stacks at 90 °C (Bülow et al., 2000). This is however
365 in contradiction with the observations of Zervos and Moropoulou who showed that the yellowing (b^*) increased
366 with time, although in much more humid exposure conditions (Zervos & Moropoulou, 2005). According to the
367 literature, the yellowing is related to chromophores arising primarily from the degradation of lignin and, to a
368 lower extent, of cellulose (Korntner et al., 2015; Menart et al., 2011). The stronger yellowing of permanent paper
369 compared to Whatman can be explained by the presence of residual lignin, as evidenced by the Kappa number of
370 2.6.



371

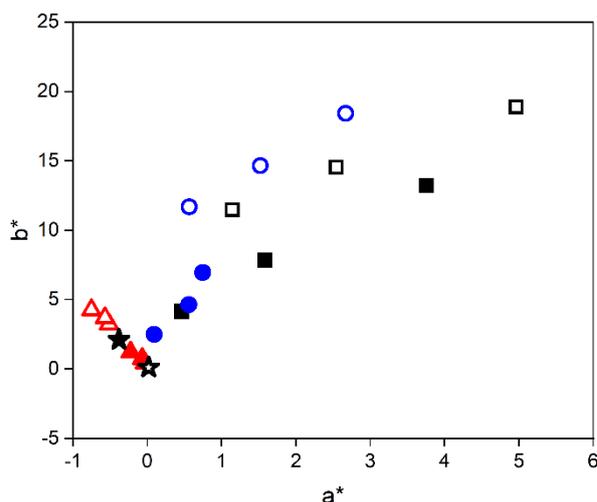
372 **Figure 6.** L*a*b* coordinates as a function of time for Whatman paper (a) and permanent paper (b).

373

374 The coloration of the paper is not directly correlated with cellulose scissions but was shown to depend on the
 375 ageing conditions. In particular, b* of permanent paper aged in humid air and humid nitrogen
 376 superimposed despite the different cellulose scission rate. Dry air condition led to the lowest coloration, which is
 377 in contradiction to a yellowing driven by oxidation of the cellulose chains (Ahn et al., 2019; Łojewska et al.,
 378 2007). Pre-oxidation of the papers before the ageing could explain the fact that only water would be needed to
 379 complete the formation of chromophoric products. Oxidative conditions could also induce a counteracting effect
 380 of chromophores degradation and subsequent disappearance of the yellowing.

381 Interestingly, a* coordinate of both papers showed a trend towards red for humid conditions and towards green
 382 for dry air conditions. Horst also found a tendency to greening in the case of deacidified papers naturally aged
 383 under humid air conditions (Horst et al., 2020). Given the fact that several chromophores may be formed during
 384 degradation (Arts et al., 1997; Korntner et al., 2015; Rosenau et al., 2005), it can be assumed that different
 385 conditions lead to different chromophores. By plotting the two coordinates a* and b* on the same graph, the
 386 colour is uniquely defined (**Figure 7**). The correlation between a* and b* accounts for a colour whose
 387 concentration increases with degradation. A colour is defined by a group of chromophores at a given proportion
 388 produced at a same rate. Given the different slopes on **Figure 7**, it appears that humid conditions led to one

389 group of chromophores, and dry air to another. Either two distinct pathways produce the two groups, or the same
390 mechanisms account for the chromophores production, and some of the chromophores are subsequently
391 degraded depending on the conditions. These mechanisms having their own kinetics, the coloration of paper
392 under archival conditions cannot be extrapolated from cellulose degradation.



393
394 **Figure 7.** Correlation between the colour coordinates a^* and b^* (initial values ★, humid air ■, humid nitrogen ●, dry air ▲; empty symbols
395 for Whatman paper and full symbols for permanent paper).

397 4. CONCLUSION

398 In conclusion, three different accelerated ageing conditions were successfully established thanks to a method that
399 was able to maintain stable conditions for prolonged periods. The absence of flows was achieved for 70 days
400 demonstrating the reproducibility of the ageing. This method enabled to determine the rate of cellulose
401 degradation at 90 °C under humid air, humid nitrogen, and dry air.

402 Both papers were sensitive to humidity and oxidation, and a synergetic process between water and oxygen was
403 exhibited. Permanent paper degradation rate was reduced in all the conditions compared to Whatman paper, and
404 more considerably so in humid conditions. As a result, if the rate of degradation in dry air conditions is about
405 five times lower than in humid nitrogen for Whatman paper, it turns out to be of the same order of magnitude for
406 permanent paper. Oxidation cannot be neglected, even in archival conditions.

407 Acidification of the permanent paper was slower compared to Whatman paper, as expected from the presence of
408 an alkaline reserve in the former. However, as the *AR* consumption was not detectible, the neutralization reaction

409 between calcium carbonate and acids was either partial or slower than the acids production. The heterogeneity of
410 the reaction between a solid phase and volatile compounds could be held responsible for this observation.

411 The coloration of paper was dependent on the ageing conditions. Indeed, for both papers, a yellowing towards
412 red was observed in the presence of water, and towards green in dry air. These colours characterize two different
413 groups of chromophores. These could be produced either by a condition-dependent reaction scheme or by a
414 preferential degradation of some types of chromophores over others whether in the presence of water or dry air.

415 In summary, we have demonstrated that both oxygen and acid-driven reactions are reduced for permanent paper
416 compared to acidic cotton paper. We report no difference in the chemical and physical consequences of the
417 degradation between the two papers, showing that the degradation mechanisms follow the same route but with
418 different kinetics.

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422 **APPENDIX. A – Water vapour flows estimation**

423 1. Increase of relative humidity in the control tubes

$$424 \quad n_{RH} = P_{\text{sat}} \cdot V/RT \cdot (RH_{\text{after}} - RH_{\text{before}}) \quad (\text{A.1})$$

425 with:

- 426 • n_{RH} the quantity of water corresponding to the RH increase per tube
- 427 • P_{sat} the equilibrium vapour pressure of water at 70 °C, *i.e.* 31.2 kPa
- 428 • V the total volume of the tube, *i.e.* 15 cL
- 429 • T the temperature of the experiment, *i.e.* 343 K
- 430 • RH_{before} and RH_{after} the relative humidity in the tube at 0 and 70 days of ageing respectively, as
431 measured by hygro buttons, *i.e.* 0.49 % and 0.52 %

433 2. Release of water thought EMC evolution

$$434 \quad n_{EMC} = (EMC_{\text{before}} - EMC_{\text{after}}) \cdot m_{\text{paper}} / M_{\text{water}} \quad (\text{A.2})$$

435 with:

- 436 • n_{EMC} the quantity of water released by the paper during ageing
- 437 • EMC_{before} and EMC_{after} the equilibrium moisture content in paper at 0 and 70 days of ageing
- 438 respectively, as measured by DVS, *i.e.* 4.22 % and 4.17 %
- 439 • m_{paper} the total mass of paper per tube, *i.e.* 4.22 g
- 440 • M_{water} the molar mass of water, *i.e.* 18 g·mol⁻¹

441 These DVS measurements were conducted in the ageing conditions, *i.e.*, 70 °C and 50 % RH, in
 442 sorption regime.

443 3. Consumption of water through hydrolysis reaction

$$444 \quad n_s = (1/DP_{70} - 1/DP_0) \cdot m_{cellulose} / M_{cellulose} \quad (\mathbf{A.3})$$

445 with:

- 446 • n_s the quantity of cellulose scissions per tube, equivalent to the quantity of water consumed
- 447 • DP_0 and DP_{70} the degree of polymerisation of cellulose at 0 and 70 days of ageing,
- 448 respectively, *i.e.* 360 and 310
- 449 • $m_{cellulose}$ the total mass of cellulose per tube, *i.e.* 4.0 g
- 450 • $M_{cellulose}$ the molar mass of cellulose, *i.e.* 162 g·mol⁻¹

451

452 4. Estimation of water vapour flows

$$453 \quad n_{flows} = n_{EMC} - n_{RH} \quad (\mathbf{A.4})$$

454 with n_{flows} the quantity of water that might have leaked outside the tube

455 **APPENDIX. B – Deviation index**

456 The deviation index *DI* used to determine the reproducibility of the ageing method is calculated as the
 457 standard deviation of the b* colour-coordinate measurements for both tubes of a same ageing condition over
 458 the mean standard deviation of the b* values of a single tube. Ten measurements were used for every
 459 standard deviation calculation:

$$460 \quad DI = 2\Delta_{10,mix} / (\Delta_{10,tube1} + \Delta_{10,tube2}) \quad (\mathbf{B.1})$$

461 with:

- 462 • $\Delta_{10,mix}$ the standard deviation of ten b^* measurements on paper randomly issued of tube 1 or 2
- 463 • $\Delta_{10,tubei}$ the standard deviation of ten b^* measurements on paper issued of tube i
- 464 • Tube 1 and tube 2 being aged in the same condition, paper, and time.

465

466 REFERENCES

- 467 Ahn, K., Henniges, U., Banik, G., & Potthast, A. (2012). Is cellulose degradation due to β -elimination processes
468 a threat in mass deacidification of library books? *Cellulose*, 19(4), 1149-1159.
469 <https://doi.org/10.1007/s10570-012-9723-3>
- 470 Ahn, K., Rosenau, T., & Potthast, A. (2013). The influence of alkaline reserve on the aging behavior of book
471 papers. *Cellulose*, 20(4), 1989-2001. <https://doi.org/10.1007/s10570-013-9978-3>
- 472 Ahn, K., Zaccaron, S., Zwirchmayr, N. S., Hettegger, H., Hofinger, A., Bacher, M., Henniges, U., Hosoya, T.,
473 Potthast, A., & Rosenau, T. (2019). Yellowing and brightness reversion of celluloses : CO or COOH,
474 who is the culprit? *Cellulose*, 26(1), 429-444. <https://doi.org/10.1007/s10570-018-2200-x>
- 475 Arney, J. S., Jacobs, A. J., & Newman, R. (1980). The influence of deacidification on the deterioration of paper.
476 *Journal of the American Institute for Conservation*, 19, 34-41. <https://doi.org/10.2307/3179571>
- 477 Arts, S. J. H. F., Mombarg, E. J. M., van Bekkum, H., & Sheldon, R. A. (1997). Hydrogen peroxide and oxygen
478 in catalytic oxidation of carbohydrates and related compounds. *Synthesis*, 597-613.
- 479 Barrow, W. J., & Sproull, R. C. (1959). Permanence in Book Papers. *Science*, 129(3356), 1075-1084.
480 <http://www.jstor.org/stable/1756742>
- 481 Baty, J., Maitland, C., Minter, W., Hubbe, M., & Jordan-Mowery, S. (2010). Deacidification for the conservation
482 and preservation of paper-based works : A review. *BioResources*, 5(3), 1955-2023.
483 <https://doi.org/10.15376/biores.5.3.1955-2023>
- 484 Bégin, P., Deschâtelets, S., Grattan, D., Gurnagul, N., Iraci, J., Kaminska, E., Woods, D., & Zou, X. (1998). The
485 Impact of Lignin on Paper Permanence. *Restaurator*, 19, 135-154.
486 <https://doi.org/10.1515/rest.1998.19.3.135>
- 487 Bégin, P. L., & Kaminska, E. (2002). Thermal Accelerated Ageing Test Method Development. *Restaurator*, 23(2),
488 89-105. <https://doi.org/10.1515/REST.2002.89>

- 489 Brillard, A., Habermacher, D., & Brilhac, J.-F. (2017). Thermal degradations of used cotton fabrics and of
490 cellulose: Kinetic and heat transfer modeling. *Cellulose*, 24(3), 1579-1595.
491 <https://doi.org/10.1007/s10570-017-1200-6>
- 492 Bülow, A., Bégin, P., Carter, H., & Burns, T. (2000). Migration of Volatile Compounds through Stacked Sheets
493 of Paper during Accelerated Ageing Part II: Variable Temperature Studies. *Restaurator*, 21(4), 187-203.
494 <https://doi.org/10.1515/REST.2000.187>
- 495 Calvini, P. (2005). The Influence of Levelling-off Degree of Polymerisation on the Kinetics of Cellulose
496 Degradation. *Cellulose*, 12(4), 445-447. <https://doi.org/10.1007/s10570-005-2206-z>
- 497 Calvini, P. (2012). The role of the Ekenstam equation on the kinetics of cellulose hydrolytic degradation. *Cellulose*,
498 19(2), 313-318. <https://doi.org/10.1007/s10570-011-9645-5>
- 499 Calvini, P., Gorassini, A., & Merlani, A. L. (2008). On the kinetics of cellulose degradation: Looking beyond the
500 pseudo zero order rate equation. *Cellulose*, 15(2), 193-203. <https://doi.org/10.1007/s10570-007-9162-8>
- 501 Carter, H., Bégin, P., & Grattan, D. (2000). Migration of Volatile Compounds through Stacked Sheets of Paper
502 during Accelerated Ageing – Part 1: Acid Migration at 90° C. *Restaurator*, 21(2), 77-84.
503 <https://doi.org/10.1515/REST.2000.77>
- 504 Ding, H.-Z., & Wang, Z. D. (2008). On the degradation evolution equations of cellulose. *Cellulose*, 15(2), 205-224.
505 <https://doi.org/10.1007/s10570-007-9166-4>
- 506 Driemeier, C., Mendes, F. M., & Oliveira, M. M. (2012). Dynamic vapor sorption and thermoporometry to probe
507 water in celluloses. *Cellulose*, 19(4), 1051-1063. <https://doi.org/10.1007/s10570-012-9727-z>
- 508 Dupont, A.-L. (2003). Cellulose in lithium chloride/N,N-dimethylacetamide, optimisation of a dissolution method
509 using paper substrates and stability of the solutions. *Polymer*, 44(15), 4117-4126.
510 [https://doi.org/10.1016/S0032-3861\(03\)00398-7](https://doi.org/10.1016/S0032-3861(03)00398-7)
- 511 Dupont, A.-L., Egasse, C., Morin, A., & Vasseur, F. (2007). Comprehensive characterisation of cellulose- and
512 lignocellulose-degradation products in aged papers: Capillary zone electrophoresis of low-molar mass
513 organic acids, carbohydrates, and aromatic lignin derivatives. *Carbohydrate Polymers*, 68(1), 1-16.
514 <https://doi.org/10.1016/j.carbpol.2006.07.005>
- 515 Dupont, A.-L., Réau, D., Bégin, P., Paris-Lacombe, S., Tétreault, J., & Mortha, G. (2018). Accurate molar masses
516 of cellulose for the determination of degradation rates in complex paper samples. *Carbohydrate Polymers*,
517 202, 172-185. <https://doi.org/10.1016/j.carbpol.2018.08.134>

- 518 Ekenstam, A. (1936). The behaviour of cellulose in mineral acid solutions : Kinetic study of the decomposition of
519 cellulose in acid solutions. *Chemische Berichte*, 69, 553.
- 520 Emsley, A. M., Heywood, R. J., Xiao, X., & Ali, M. (2000). Degradation of cellulosic insulation in power
521 transformers. Part 3 : Effects of oxygen and water on ageing in oil. *IEE Proceedings - Science,*
522 *Measurement and Technology*, 147(3), 115-119. <https://doi.org/10.1049/ip-smt:20000021>
- 523 Gehlen, M. H. (2010). Kinetics of autocatalytic acid hydrolysis of cellulose with crystalline and amorphous
524 fractions. *Cellulose*, 17(2), 245-252. <https://doi.org/10.1007/s10570-009-9385-y>
- 525 Glaus, M. A., & Van Loon, L. R. (2008). Degradation of Cellulose under Alkaline Conditions : New Insights from
526 a 12 Years Degradation Study. *Environmental Science & Technology*, 42(8), 2906-2911.
527 <https://doi.org/10.1021/es7025517>
- 528 Glaus, M. A., Van Loon, L. R., Achatz, S., Chodura, A., & Fischer, K. (1999). Degradation of cellulosic materials
529 under the alkaline conditions of a cementitious repository for low and intermediate level radioactive waste
530 Part I: Identification of degradation products. *Analytica Chimica Acta*, 398, 111-122.
531 [https://doi.org/10.1016/S0003-2670\(99\)00371-2](https://doi.org/10.1016/S0003-2670(99)00371-2)
- 532 Hill, D. J. T., Le, T. T., Darveniza, M., & Saha, T. (1995). A study of degradation of cellulosic insulation materials
533 in a power transformer, part 1. Molecular weight study of cellulose insulation paper. *Polymer*
534 *Degradation and Stability*, 48, 79-87. [https://doi.org/10.1016/0141-3910\(95\)00023-F](https://doi.org/10.1016/0141-3910(95)00023-F)
- 535 Horst, T. H., Smith, R. D., Potthast, A., & Hubbe, M. A. (2020). Accelerated Aging of Deacidified and Untreated
536 Book Paper in 1967 Compared with 52 Years of Natural Aging. *Restaurator. International Journal for*
537 *the Preservation of Library and Archival Material*, 41(3), 131-152. [https://doi.org/10.1515/res-2020-](https://doi.org/10.1515/res-2020-0006)
538 0006
- 539 Hosoya, T., Bacher, M., Potthast, A., Elder, T., & Rosenau, T. (2018). Insights into degradation pathways of
540 oxidized anhydroglucose units in cellulose by β -alkoxy-elimination : A combined theoretical and
541 experimental approach. *Cellulose*, 25(7), 3797-3814. <https://doi.org/10.1007/s10570-018-1835-y>
- 542 Hubbe, M. A., Smith, R. D., Zou, X., Katuscak, S., Potthast, A., & Ahn, K. (2017). Deacidification of Acidic
543 Books and Paper by Means of Non-aqueous Dispersions of Alkaline Particles : A Review Focusing on
544 Completeness of the Reaction. *BioResources*, 12(2), 4410-4477.
545 https://doi.org/10.15376/biores.12.2.Acidic_Books_Hubbe
- 546 Jeong, M.-J., & Potthast, A. (2021). Improving the accuracy of estimating paper permanence for accelerated
547 degradation in closed vials. *Cellulose*, 28, 4053-4068. <https://doi.org/10.1007/s10570-021-03804-y>

- 548 Kerekes, R., & McDonald, D. (2020). Equilibrium moisture content in wet pressing of paper. *TAPPI Journal*,
549 19(7), 330-340. <https://doi.org/10.32964/TJ19.7.333>
- 550 Knill, C. J., & Kennedy, J. F. (2003). Degradation of cellulose under alkaline conditions. *Carbohydrate Polymers*,
551 51(3), 281-300. [https://doi.org/10.1016/S0144-8617\(02\)00183-2](https://doi.org/10.1016/S0144-8617(02)00183-2)
- 552 Kolar, J. (1997). Mechanism of Autoxidative Degradation of Cellulose. *Restaurator*, 18(4), 163-176.
553 <https://doi.org/10.1515/rest.1997.18.4.163>
- 554 Korntner, P., Hosoya, T., Dietz, T., Eibinger, K., Reiter, H., Spitzbart, M., Röder, T., Borgards, A., Kreiner, W.,
555 Mahler, A. K., Winter, H., Groiss, Y., French, A. D., Henniges, U., Potthast, A., & Rosenau, T. (2015).
556 Chromophores in lignin-free cellulosic materials belong to three compound classes. Chromophores in
557 cellulose, XII. *Cellulose*, 22(2), 1053-1062. <https://doi.org/10.1007/s10570-015-0566-6>
- 558 Łojewska, J., Missori, M., Lubańska, A., Grimaldi, P., Zięba, K., Proniewicz, L. M., & Congiu Castellano, A.
559 (2007). Carbonyl groups development on degraded cellulose. Correlation between spectroscopic and
560 chemical results. *Applied Physics A*, 89(4), 883-887. <https://doi.org/10.1007/s00339-007-4220-5>
- 561 Lundgaard, L. E., Hansen, W., Ingebrigtsen, S., Linhjell, D., & Dahlund, M. (2005). Aging of kraft paper by acid
562 catalyzed hydrolysis. *IEEE International Conference on Dielectric Liquids, 2005. ICDL 2005.*, 375-378.
563 <https://doi.org/10.1109/ICDL.2005.1490105>
- 564 Mäki-Arvela, P., Salmi, T., Holmbom, B., Willför, S., & Murzin, D. Yu. (2011). Synthesis of Sugars by Hydrolysis
565 of Hemicelluloses- A Review. *Chemical Reviews*, 111(9), 5638-5666. <https://doi.org/10.1021/cr2000042>
- 566 Malesic, J., Kolar, J., & Strlič, M. (2002). Effect of pH and Carbonyls on the Degradation of Alkaline Paper Factors
567 Affecting Ageing of Alkaline Paper. *Restaurator*, 23(3), 145-153.
568 <https://doi.org/10.1515/REST.2002.145>
- 569 Margutti, S., Conio, G., Calvini, P., & Pedemonte, E. (2001). Hydrolytic and Oxidative Degradation of Paper.
570 *Restaurator*, 22(2), 67-83. <https://doi.org/10.1515/REST.2001.67>
- 571 Menart, E., De Bruin, G., & Strlič, M. (2011). Dose–response functions for historic paper. *Polymer Degradation
572 and Stability*, 96(12), 2029-2039. <https://doi.org/10.1016/j.polymdegradstab.2011.09.002>
- 573 Nevell, T. P., & Zeronian, S. H. (1985). *Cellulose Chemistry and its Applications* (Ellis Horwood).
574 10.1002/pol.1987.140250212
- 575 Poggi, G., Toccafondi, N., Melita, L. N., Knowles, J. C., Bozec, L., Giorgi, R., & Baglioni, P. (2014). Calcium
576 hydroxide nanoparticles for the conservation of cultural heritage: New formulations for the

- 577 deacidification of cellulose-based artifacts. *Applied Physics A*, 114, 685-693.
578 <https://doi.org/10.1007/s00339-013-8172-7>
- 579 Potthast, A., Rosenau, T., Kosma, P., Saariaho, A.-M., & Vuorinen, T. (2005). On the Nature of Carbonyl Groups
580 in Cellulosic Pulps. *Cellulose*, 12(1), 43-50. <https://doi.org/10.1023/B:CELL.0000049347.01147.3d>
- 581 Rånby, B. G. (1961). "Weak links" in polysaccharide chains as related to modified groups. *Journal of Polymer*
582 *Science*, 53(158), 131-140. <https://doi.org/10.1002/pol.12005315819>
- 583 Rosenau, T., Potthast, A., Kosma, P., Hosoya, T., Henniges, U., Mereiter, K., & French, A. D. (2017). 2,4':2',4
584 Dianhydride of 3-keto-glucoside, a precursor to chromophores of aged, yellow cellulose, and its weak
585 interactions. *Cellulose*, 24(3), 1227-1234. <https://doi.org/10.1007/s10570-017-1198-9>
- 586 Rosenau, T., Potthast, A., Milacher, W., Adorjan, I., Hofinger, A., & Kosma, P. (2005). Discoloration of cellulose
587 solutions in N-methylmorpholine-N-oxide (Lyocell). Part 2: Isolation and identification of
588 chromophores. *Cellulose*, 12(2), 197-208. <https://doi.org/10.1007/s10570-004-0210-3>
- 589 Sawoszczuk, T., Barański, A., Łagan, J. M., Łojewski, T., & Zięba, K. (2008). On the use of ASTM closed vessel
590 tests in accelerated ageing research. *Journal of Cultural Heritage*, 9(4), 401-411.
591 <https://doi.org/10.1016/j.culher.2007.10.010>
- 592 Stephens, C. H., Whitmore, P. M., Morris, H. R., & Bier, M. E. (2008). Hydrolysis of the Amorphous Cellulose
593 in Cotton-Based Paper. *Biomacromolecules*, 9(4), 1093-1099. <https://doi.org/10.1021/bm800049w>
- 594 Tétreault, J., Bégin, P., Paris-Lacombe, S., & Dupont, A.-L. (2019). Modelling considerations for the degradation
595 of cellulosic paper. *Cellulose*, 26(3), 2013-2033. <https://doi.org/10.1007/s10570-018-2156-x>
- 596 Wilson, W. K., & Parks, E. J. (1979). An Analysis of the Aging of Paper : Possible Reactions and their Effects on
597 Measurable Properties. *Restorator*, 3, 37-62. <https://doi.org/10.1515/rest.1979.3.1-2.37>
- 598 Zervos, S., & Moropoulou, A. (2005). Cotton Cellulose Ageing in Sealed Vessels. Kinetic Model of Autocatalytic
599 Depolymerization. *Cellulose*, 12(5), 485-496. <https://doi.org/10.1007/s10570-005-7131-7>
- 600 Zou, X., Gurnagul, N., & Uesaka, T. (1993). The role of lignin in the mechanical permanence of Paper—Part I:
601 Effect of lignin content. *Journal of pulp and paper science*, 19(6), 235-239.
- 602 Zou, X., Gurnagul, N., Uesaka, T., & Bouchard, J. (1994). Accelerated aging of papers of pure cellulose :
603 Mechanism of cellulose degradation and paper embrittlement. *Polymer Degradation and Stability*, 43(3),
604 393-402. [https://doi.org/10.1016/0141-3910\(94\)90011-6](https://doi.org/10.1016/0141-3910(94)90011-6)
- 605