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

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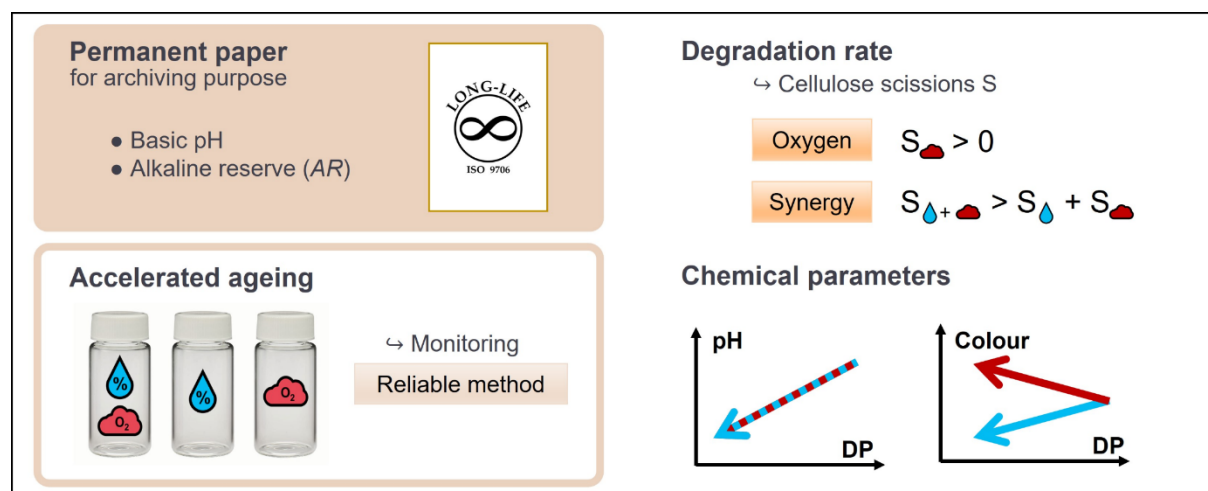
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**Keywords:** Accelerated aging; Kinetics; Acidification; Alkaline reserve; Degree of polymerization; Coloration

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



## 1. INTRODUCTION

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

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

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

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

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

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

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

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

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

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

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

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

## 2. MATERIALS AND METHODS

### 2.1. Paper samples

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

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

Paper	Fibres	Grammage (g·m <sup>-2</sup> )	pH	AR (%)	Kappa number	EMC (%)	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

### 2.2. Accelerated ageing

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

Samples were aged in 15 cL Wheaton® glass tubes. 4.00 ± 0.01 g equivalent of dry paper cut in strips (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 were closed with a polypropylene screw cap and a PTFE septum (Duran Groups®, max. 140 °C). A three-layered gas impermeable film (IN SITU Museum & Archive Services®, PET, aluminium and polyethylene) was added between the tube and the septum.

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

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

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

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

**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

### 2.3. Analytical characterization

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

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

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

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

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

### 3. RESULTS AND DISCUSSION

#### 3.1. Validation of the accelerated ageing method

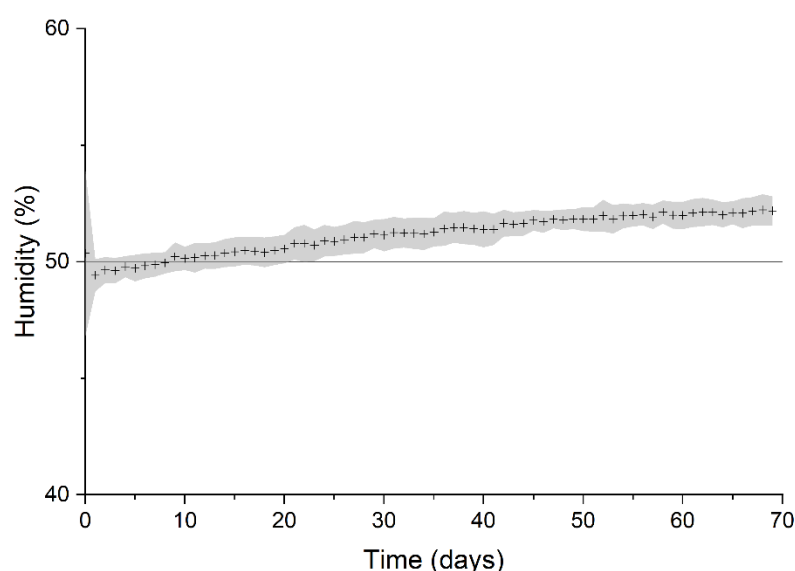
The experimental work was based on the accelerated ageing of two different types of paper under three ageing conditions to discriminate the role of water and oxygen on the degradation of permanent and acidic paper. To ensure the reliability of the results, the accelerated ageing method was tested through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



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

### 3.1.1. Monitoring of the relative humidity inside the tubes

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



**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, standard deviation in grey.

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

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

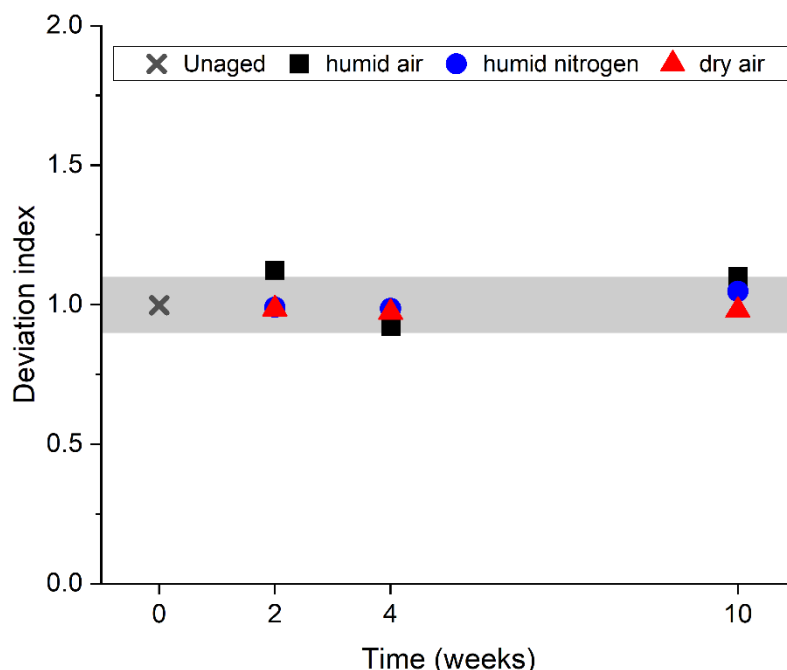
Interestingly, other authors showed an important drop of  $RH$  during ageing in closed vials at similar temperature, with a decrease of 30 % in 80 days at 65 °C (Jeong & Potthast, 2021). They linked this decrease with the presence of water vapour flows outside the closed vials and, as the concentration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

### 3.1.2. Reproducibility of the ageing method

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

$DI$  is plotted **Figure 2** for each condition and duration.  $DI$  was close to 1 in all cases, showing that there was no significant difference between two replicate tubes aged in the same conditions. The index did not increase with 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  $DI = 1 \pm 10\%$ .

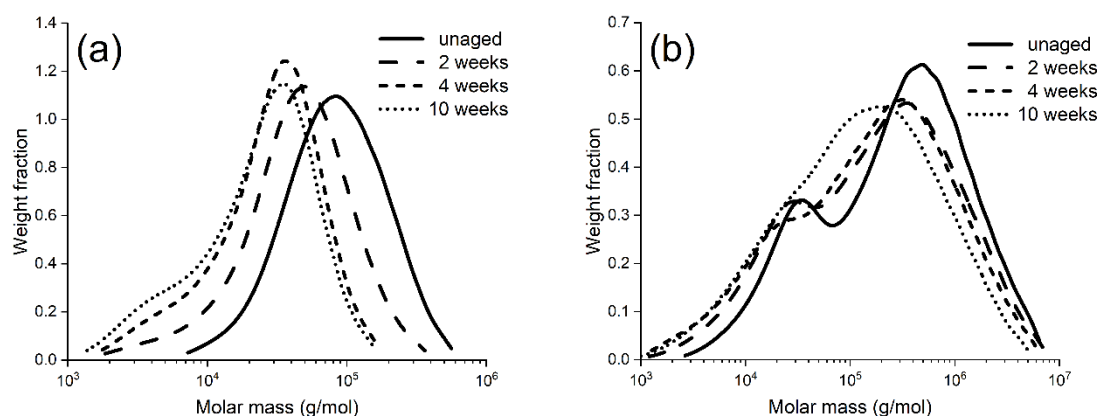
232 All in all, the accelerated ageing method used in this study was robust and reproducible, as no flow was  
 233 evidenced in 10 weeks. Water was the only assessed parameter for flows evaluation, but it can be assumed that  
 234 neither oxygen, nitrogen nor volatile acid compounds could flow during 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

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



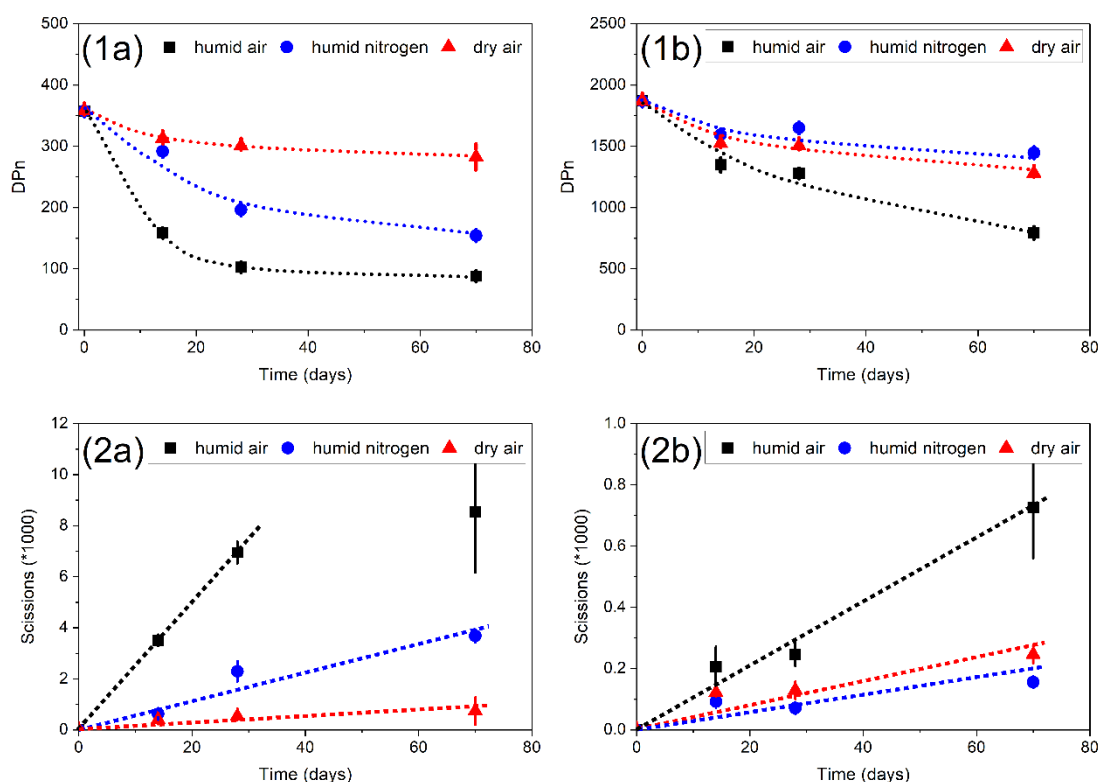
**Figure 3.** Molar mass distribution for the Whatman paper (a) and permanent paper (b) aged under humid air condition for different ageing times.

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

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 similar and shows a maximal decrease rate at the beginning of the ageing, followed by a deceleration for longer exposure times. This shape is characteristic for cellulose ageing (Tétreault et al., 2019; Zou et al., 1994). In humid air conditions,  $DP_n$  decreased by 60 % for Whatman paper and by 30 % for permanent paper. For both papers, the 10-week ageing is sufficient to reach a significant degradation state, allowing further comparisons of the  $DP_n$  evolution.

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

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



**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 glucose unit (2) for Whatman paper (a) and permanent paper (b)

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

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

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

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

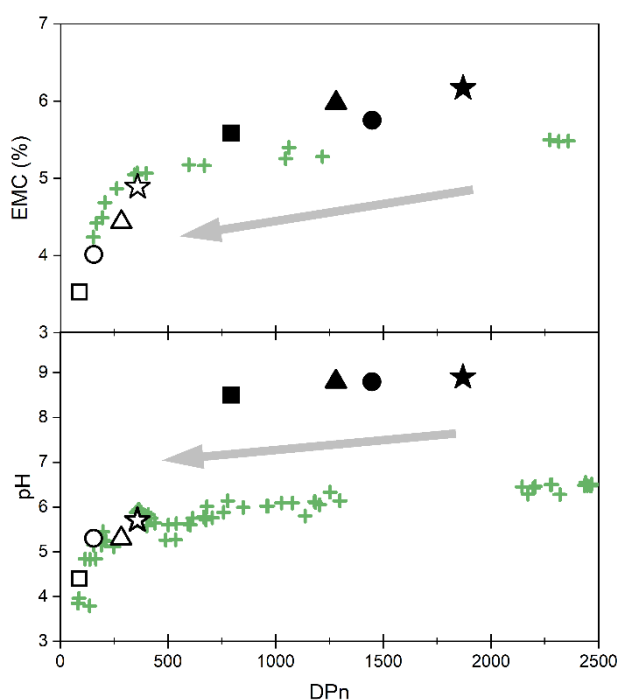
Paper	Ageing conditions	$k (\times 10^6 \text{ day}^{-1})$	<i>EMC</i> at 30 °C (%)	pH	<i>AR</i> (%)
Whatman	<i>unaged</i>	/	4.9	5.7	/
	humid air	$250 \pm 1.4$	3.5	4.4	/
	humid nitrogen	$56 \pm 11.8$	4.0	5.3	/
	dry air	$12 \pm 4.8$	4.4	5.3	/
permanent	<i>unaged</i>	/	6.2	8.9	3.3
	humid air	$10 \pm 1.2$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

### 3.3. Macroscopic changes

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

#### 3.3.1. Water content

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



**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 ■, humid nitrogen ●, dry air ▲; empty symbols for Whatman paper and full symbols for permanent paper). Literature data for acidic and neutral cotton paper are superimposed (in green crosses, data from [Tétreault et al., 2019]). The progress of ageing is indicated by the arrows.

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

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

### 3.3.2. Acidification

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

The acidification is linear with the decrease in  $DP_n$  for each paper, depending only slightly on the degradation conditions (**Figure 5**). For Whatman paper, the values superimposed well with T  treault's data, and other studies on the same paper have also shown similar acidification (T  treault et al., 2019; Zervos & Moropoulou, 2005). For the permanent paper, as expected, acidification is slower, as shown by the lower slope.

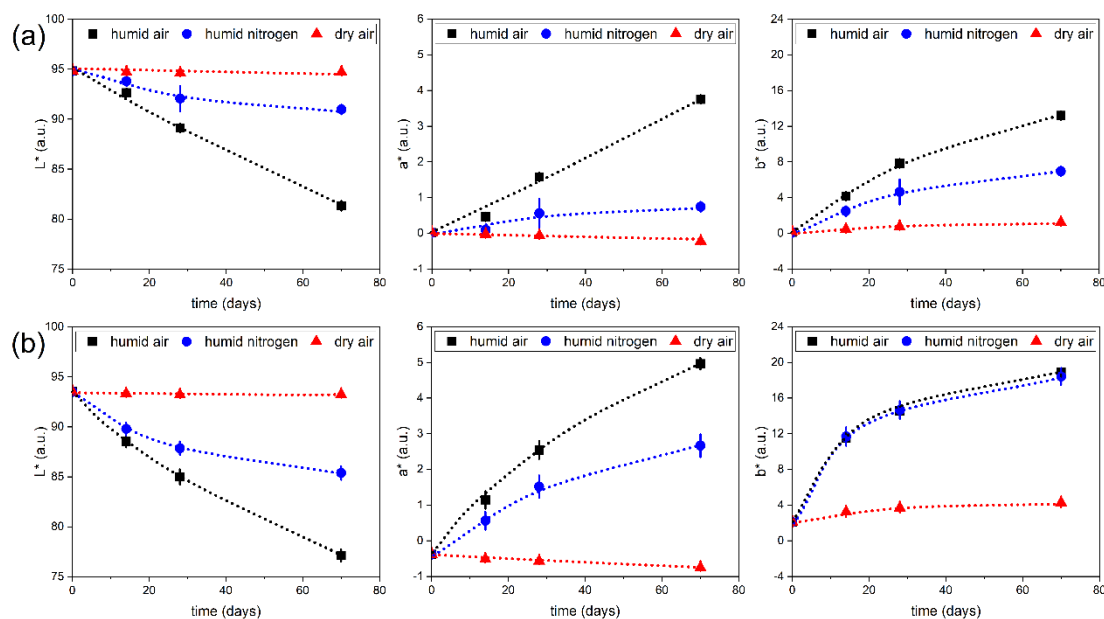
The presence of alkaline reserve (*AR*) in permanent paper is supposed to neutralize the acids formed during the degradation (Ahn et al., 2013; B  gin et al., 1998; Poggi et al., 2014). For this reason, the *AR* of permanent paper after ageing was investigated (**Table 3**). No consumption of the *AR* was detectable. This might be explained by a large excess of alkaline content, overriding its consumption. This hypothesis was tested by calculating the production of acids and comparing to the alkaline reserve. Let us consider the number of acids formed per cellulose scission in Whatman paper as reference. Under the 10-week humid air ageing, around  $4 \times 10^{-5} \text{ mol} \cdot \text{g}^{-1}$  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 scission. Considering permanent paper, the number of scissions under the same conditions is  $4 \times 10^{-6} \text{ mol} \cdot \text{g}^{-1}$ , assuming that cellulose and hemicelluloses have a similar hydrolysis rate and represent the whole dry mass (M  ki-Arvela et al., 2011). According to the acids production ratio determined for Whatman paper, it is 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 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 formation.



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

### 3.3.3. Coloration

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

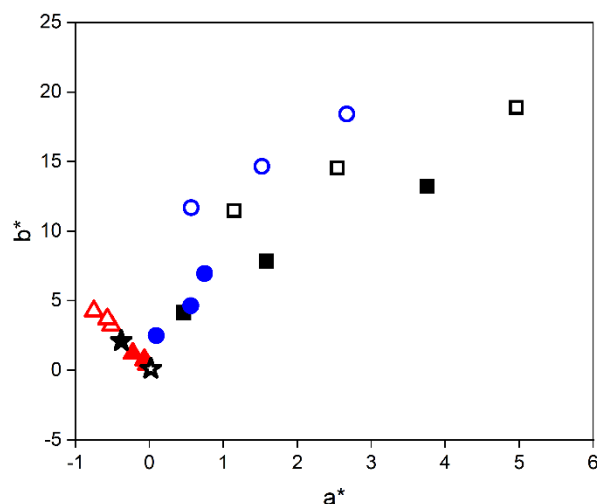


**Figure 6.**  $L^*a^*b^*$  coordinates as a function of time for Whatman paper (a) and permanent paper (b).

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

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

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



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

#### 4. CONCLUSION

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

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

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

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

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

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

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## APPENDIX. A – Water vapour flows estimation

### 1. Increase of relative humidity in the control tubes

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

with:

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

### 2. Release of water through $EMC$ evolution

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

with:

- $n_{\text{EMC}}$  the quantity of water released by the paper during ageing
- $\text{EMC}_{\text{before}}$  and  $\text{EMC}_{\text{after}}$  the equilibrium moisture content in paper at 0 and 70 days of ageing respectively, as measured by DVS, *i.e.* 4.22 % and 4.17 %
- $m_{\text{paper}}$  the total mass of paper per tube, *i.e.* 4.22 g
- $M_{\text{water}}$  the molar mass of water, *i.e.* 18 g·mol<sup>-1</sup>

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

### 3. Consumption of water though hydrolysis reaction

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

with:

- $n_s$  the quantity of cellulose scissions per tube, equivalent to the quantity of water consumed
- $DP_0$  and  $DP_{70}$  the degree of polymerisation of cellulose at 0 and 70 days of ageing, respectively, *i.e.* 360 and 310
- $m_{\text{cellulose}}$  the total mass of cellulose per tube, *i.e.* 4.0 g
- $M_{\text{cellulose}}$  the molar mass of cellulose, *i.e.* 162 g·mol<sup>-1</sup>

### 4. Estimation of water vapour flows

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

with  $n_{\text{flows}}$  the quantity of water that might have leaked outside the tube

## APPENDIX. B – Deviation index

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

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

with:

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

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