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Mass deacidification of papers and books. IV – A study of papers treated with aminoalkylalkoxysilanes and their resistance to ageing

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Abstract

In libraries and archives some of the time-acidified items are so brittle that they cannot be handled without risking loss of material. Currently used deacidification processes do not impart improved mechanical properties to the paper. The use of alcoholic solutions of three different types of aminoalkylalkoxysilanes was studied for the deacidification of paper-based items. It was shown that in addition to deacidifying and improving the stability of papers by providing an alkaline buffer the treatment also significantly improved their mechanical resistance, as measured by the folding endurance and tensile breaking resistance. Essential for the appraisal of the deacidification process, the behaviour upon ageing of the materials treated was investigated. Accelerated ageing methods involving heat/humidity and nitrogen dioxide atmosphere were used separately. It was shown that the reinforcement effect of the three aminosilane compounds tested persisted throughout the ageing, and in one case the mechanical properties even improved after ageing. Two of the aminosilanes tested were studied for their impact at the macromolecular level, on the molar masses of cellulose, using size-exclusion chromatography with multiangle light scattering detection. Their effectiveness in protecting paper from acid hydrolysis occurring during ageing was found significant.

Keywords: Aminosilane; Paper; Cellulose; Deacidification; Reinforcement; Ageing

1. Introduction

Mass deacidification is a key issue for libraries and archives trying to ensure the long-term preservation of items on acidic paper, and it is often the sole conservation treatment solution for a wide range of books pertaining to 19th–20th century collections. Indeed, ultimately acidic paper becomes brittle and unusable. Mass deacidification is a chemical process involving the neutralisation of the acids present in the paper and the deposition of an alkaline buffer to prevent, or at least retard, further acidification. However, it is still a controversial question and the main reproach made to current processes is that besides the neutralisation and buffering action there is no physical strengthening of the paper.

In a previous publication [1], a process using an ethanolic solution of aminoalkylalkoxysilane was described. It was shown that paper that had been in contact with 3-aminopropyltrimethoxysilane or similar aminosilanes could efficiently deacidify while an alkaline buffer (called AR) could simultaneously deposit in the cellulosic network. Considering that the treatment relies on the reactivity of amine functions, mainly primary amines, it is necessary to investigate the resistance to ageing of the treated materials, which is essential for the appraisal of the deacidification process. An examination of

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paper samples treated with aminoalkylalkoxysilanes (further on called aminosilanes for the sake of simplicity), after accelerated ageing, would give an idea of the resistance of the items to long-term storage in ordinary libraries. As noted earlier, the main cause of decay of papers and books is the acid content in combination with time of exposure at room temperature. The contact with pollutants found even at low concentration in the atmosphere of libraries located in urban areas also promotes degradation. Among common atmospheric pollutants nitrogen dioxide is one of the most powerful in promoting the oxidative and hydrolytic degradation of cellulosic materials [2,3]. Based on these known facts, three separate accelerated ageing methods were chosen. In the first one an atmosphere enriched in nitrogen dioxide at room temperature was used, following ASTM standard method D6833-02E01 [4]. In the second one the ageing was promoted by an increase in temperature at high relative humidity in a ventilated climate chamber (ISO 5630-3:1996) [5]. This type of ageing has been shown to promote the degradation of cellulose via acid-catalysed hydrolysis [6–8] which induces a decrease in the degree of polymerisation (DP) of the cellulose. It has been shown more recently that during natural ageing the volatile acidic compounds generated can remain trapped in the paper, because diffusion is a slow process [9]. Indeed, papers aged in stacks degraded more rapidly and to a greater extent than those aged as single sheets. Thus, an accelerated ageing process involving the prolonged contact of papers with their degradation products can also inform on the ageing behaviour of books and stacked archives, where the central pages are kept in a confined environment on shelves. Moreover, the benefit of deacidification was more significant for samples artificially aged in stack than for individually hung sheets [9,10]. Accordingly, the third accelerated ageing method used took place at high temperature (90 °C) in sealed tubes, according to ASTM standard method D6819-02E02 [11–13]. This type of ageing, where both moisture content of paper and degradation products trapped in the confined air and in the fibres play a role, is thought to simulate more closely natural ageing [10].

In the present study, the level of penetration of deacidification agents across the sheets of paper was not measured. The homogeneity of penetration of the alkaline buffer into the paper is an important issue. In the present process, the use of an alcohol as solvent certainly favours an even distribution of the treatment product in the fibre web. This aspect of the deacidification process will be dealt within a future study. For the sake of a general appraisal, no document with iron gall ink or ancient manuscript was selected. The inherent wide variety of papers and documents present in archive collections is an aspect that could not be covered at this stage in the research.

2. Experimental

2.1. Materials

The model paper chosen (called STEP2) was a pure cellulose paper and contained no fillers or sizing. It was made of 95% cotton and 5% softwood pulp (grammage: 76 g/m^2), and had a cold water extract pH of 7.0. It was composed of a large proportion of highly ordered cellulose and consequently was less prone to swelling than papers with higher amorphous cellulose content. This characteristic allowed an easier access of the air pollutants or the acids that are formed during the ageing process to the alkaline buffer located at the surface of the crystallites [3]. The reasons for choosing paper STEP2 for the study were twofold: it had a simple composition (pure cellulose), and it had been fully characterised in a previous study (mechanical and chemical properties). Pure cellulose papers are most often neutral, and in fact, fully appropriate for size-exclusion chromatography analysis, as only pure cellulose paper dissolves well in the associated solvent. This type of paper was thus a logical choice for appraising the chemical aspects of the deacidification process at the macromolecular level.

In order to closely mimic a genuine case example, a naturally aged acidic paper from a book (named book K, 64.5 g/m^2, initial acidity = 6 meq/100 g) was used. Only mechanical testing was performed on book K as it is made of a pulp with high lignin content, which cannot be analysed easily with the SEC method used. Sixteen page fragments were treated with different aminosilanes so as to allow the comparison between the various treatments.

2.2. Treatment solutions

Three aminoalkylalkoxysilane-based treating solutions were prepared by mixing 1 L of alcohol (absolute) with 80 g of the aminosilane compound, corresponding to a concentration of 9.1% in weight. Three different aminosilane compounds were used, namely: 3-aminopropyltrimethoxysilane (ATMS) (ABCR Gelest), 3-aminopropyltriethoxysilane (ATES) (ABCR Gelest), and 4-amino-3,3-dimethylbutyltrimethoxysilane (ADBTMS) (Crompton Europe). ATES and ADBTMS have the same molar mass, thus the solutions had the same molar concentration. Ten sheets of paper were weighed and immersed for 10 min in each solution in open air. They were then slightly pressed by hand in order to eliminate the excess solution, and dried in an oven under vacuum for 3 h. Once dry, they were weighed once more in order to determine the aminosilane uptake.

2.3. Physico-chemical determinations

The Alkaline reserve (AR) was measured according to the standard method ASTM D4988-96R01 [14] in which a known quantity of HCl is added to the paper in order to react with the alkali present. NaOH is used for the back-titration of the excess HCl (the AR of a paper can be introduced either during the pulping process or, as in the present case, during a deacidification treatment).

The tensile breaking resistance was measured according to the standard method NF: Q03-004 July 1986 [15] and the folding endurance was determined according to ISO 5626:1993 [16] as mentioned in previous publications [1,17].

2.4. M_r and MMD characterisation

The molar mass (M_r) and molar mass distribution (MMD) of cellulose from STEP2 paper were determined using

size-exclusion chromatography (SEC) with dual on-line detection, multiangle laser light scattering (MALS) and differential refractive index (DRI). A LC solvent vacuum degasser 1100 series (Agilent), an isocratic HPLC pump 515 (Waters), and a manual injector (Vici AG, Valco International) were used in the chromatographic set-up. An on-line filter 0.22 μm (Millipore) was placed between the pump and the injector to filter any remaining particles in the mobile phase. The MALS detector was a Dawn EOS (Wyatt Technologies), and the DRI detector was a 2414 (Waters). The laser source of the MALS has a nominal power of 25 mW, and operates at 690 nm, the LED of the DRI emits at 880 nm. The interdetector delay volume was 0.22 mL. The constants of the instruments were experimentally determined as 7.187×10^{-6} for the MALS and 2.417×10^{-5} V^{-1} for the DRI.

The separation was carried out on a set of four columns packed with polystyrene divinyl benzene (PSDVB) Phenogel Linear(2) (5-μm particle-diameter mixed bed pores columns, $L \times D$ 300 mm × 4.6 mm, Phenomenex) preceded by a guard column Phenogel (5-μm $L \times D$ 30 mm × 4.6 mm, Phenomenex). The columns have a linear separation in the range 500 g mol^{-1} to 5×10^7 g mol^{-1}. The columns compartment (Interchim, model 102) and the MALS were thermostated at 60 °C, the DRI was set to 55 °C. The mobile phase, *N*,*N*-dimethylacetamide with 0.5% lithium chloride (LiCl/DMAc), was filtered through 0.5 μm pore Millex LCR filters (Millipore) prior to use. The system was operated at a flow rate of 0.4 mL min^{-1} with an injection volume of 100 μL, and the run time was 50 min. The dissolution of the paper samples was carried out in 8%LiCl/DMAc according to a procedure recently developed and detailed in a previous publication [18].

The data acquisition was carried out with ASTRA software version 5.1.7.3 (Wyatt Technologies) in 0.5 s intervals. The value of d*n*/d*c* of cellulose in LiCl/DMAc was previously experimentally determined as 0.077 ± 0.003 mL g^{-1}, and the second virial coefficient A_2 can be omitted in the calculations [19]. Each cellulose solution was run 2 times non-consecutively. Only the average values are reported in the tables. A repeatability study of the SEC–MALS/DRI method carried out previously yielded a RSD of 2.5% on M_w for three separate cellulose samples analysed 2–3 times non-consecutively [19].

2.5. Accelerated ageing procedures

In the first procedure, ageing of paper was carried out in suspended sheet configuration at 80 °C and 65% relative humidity (rH) for 28 days in an environmental chamber Heraeus Vöstch HC0020 according to ISO 5630-3:1996 [5]. In this procedure, the degradation products formed are forced out from the paper web by the ventilation in the chamber. The second ageing procedure was carried out according to ASTM D6819-02E02 [11]: strips of paper were placed in a tightly closed vessel which was heated to 90 °C for 14 days in a dry oven. This procedure was rather rigorous and was intended to better simulate the real situation inside a stacked book where the cellulosic web remains in contact with degradation products as they form, since the latter cannot easily diffuse through the edges and escape from the book. The humidity inside the tube was buffered with the moisture content of the paper which had been previously conditioned. The third procedure was specific to the behaviour of the items in a polluted environment, and involved a 5-day exposure to 50 ppm NO_2 at 23 °C and 50% rH, according to the ASTM D6833-02E01 [4]. The pollution chamber delivered a laminar flow of NO_2 and was controlled at both ends by a chemiluminescence analyser AC 31 M for nitrogen dioxides (Environment SA).

Prior to discussing the various aspects of the results, it is important to mention the level of precision of the values determined. Due to the good homogeneity of the paper STEP2, it was experimentally shown that the breaking length could be determined with a precision of ±5%, while the elongation at breaking was found in a ±10% range. As expected, the folding endurance was determined with a lower precision, within a ±15% range. As for the acid-base determinations, precision depends on the evenness of the treatment, *i.e.* on the homogeneity of penetration of the treatment solution between and throughout the pages. It has to be mentioned that the defibrillation of some of the treated papers was found difficult (it was necessary to defibrillate the samples prior to the acid-base titration). Thus, the precision range for these measurements was within ±10%.

3. Results and discussion

3.1. Study of the aminosilane uptake in the paper web

Alkoxysilyl functions are supposedly sensitive to moisture, *i.e.* they hydrolyse easily in the presence of water. However, once introduced in the paper web, their state of hydrolysis and the time necessary for this reaction to occur are unknown. On the other hand, the weight uptake of the aminosilane depends on its state of hydrolysis, the weight of a hydroxylic group being lower than that of an ethoxy or methoxy function. A small study was devoted to shed light on the functional state of the aminosilane in the paper web after treatment, and to evaluate the type of information obtained by the measurement of the product uptake.

Sheets of paper STEP2 were treated either with ATES or with ADBTMS. Immediately following the treatment, the AR (AR) was measured and compared with the aminosilane uptake determined by weight. It was verified that the moisture content of the papers before and after treatment was similar. Indeed for both the aminosilanes moisture content was found around 5.5%, showing that the treatment did not appreciably modify the affinity for water of the cellulosic substrate.

The results are shown in Table 1. The second column in Table 1 shows the calculated equivalent of basic function from the aminosilane uptake measured by the weight gain of the paper. The calculation of AR is based on the assumption that the aminosilane was not hydrolysed during the treatment. Conversely, the third column gives the AR assuming a complete hydrolysis of the aminosilane functions. The fourth column presents the AR as directly determined using the usual

Table 1
Aminosilane uptake of paper STEP2 alkaline reserve (meq. OH^-/100 g)

Treatment	AR calculated from uptake assuming no hydrolysis	AR calculated from uptake assuming hydrolysis	AR acid-base titration
ATES	43	70	25
ADBTMS	42	53	30

Table 2
Alkaline reserve of paper STEP2 (meq. OH^-/100 g) after treatment and ageing

Treatment solution 9.1% (w/w)	Unaged	Aged		
		80 °C/65% rH	90 °C/sealed vessel	NO_2 – 25 °C/50% rH
ATES	25	21	20	17
ADBTMS	30	32	27	22

standard experimental chemical procedure. It can be seen that the AR measured by the standard procedure was lower than the value calculated assuming no hydrolysis of the aminosilane, the latter value being lower than the AR calculated assuming a complete hydrolysis of the aminosilane. For the ADBTMS treated paper, the low value of the AR measured by acidimetry must not be assigned to the degradation of the treatment product, since, as will be shown later, the treated papers maintain a rather stable AR when kept at room temperature. It could be argued that part of the basic functions is neutralised by the initial acidity that is present in the paper before treatment. However, this cannot be the case for STEP2 samples, as this paper does not exhibit such acidity. Thus, the explanation proposed for this phenomenon is related to the formation of a fraction of cross-linked particles inside the paper web, which would prevent part of the amine functions from being titrated. This result shows that the standard titration procedure is not adapted to this type of alkalinity, and most probably leads to an underestimated value of the AR. This is not surprising because upon hydrolysis multifunctional silanes yield silanetriol functions leading to a cross-linked material. This material likely cannot be totally neutralised in the titration process due to the lack of exchange between the cross-linked particles and the titrating solution. The difference between the AR measured by the weight uptake and the AR directly determined by acidimetry has often been observed to vary all along this research work. The reason can lie in the fact that the titration is carried out in a heterogeneous medium. As mentioned earlier the difficulty found in defibrillating some of the treated papers would tend to confirm the hypothesis that the interpenetrating poly(siloxane) network is tightly cross-linked [17].

3.2. Study of the ageing behaviour of the treated papers

Ageing behaviour is an important aspect of the appraisal of mass deacidification using aminosilanes. The results of the AR determinations after the three different ageing processes are shown in Table 2. The paper treated by ATES seemed to present approximately the same fair resistance to the hydrolytic-driven types of ageing (columns 3 and 4, Table 2). The paper still contained an AR of 20 meq/100 g after 14 days at 90 °C in a sealed vessel, starting from an initial content of 25 meq/100 g. It must be underlined that 20 meq/100 g AR corresponds to 1% (wt/wt) $CaCO_3$ (units more commonly used by the conservation specialist). This result means that the amino groups were not degraded rapidly by the exposure to high temperature. It shows that the basic functions responsible for the AR are quite stable. The ageing in sealed vessel seemed only slightly more aggressive than the heat/humid ageing in the environmental chamber. The oxidative-driven ageing by exposure to NO_2 for 5 days (column 5, Table 2) was found slightly more detrimental to the AR with a loss of 8 meq/100 g.

The paper presented overall similar behaviour when treated with ADBTMS and when treated with ATES, although the AR obtained was slightly better with the ADBTMS treatment depending on the ageing process. The loss of AR after 28 days at 80 °C and 65% rH was completely negligible. Upon exposure to NO_2 the loss of AR was small (loss of 8 meq/100 g for both papers).

The main mechanism leading to the decrease in the alkaline reserve is discussed farther on. At first sight, the stability of the amino groups needs to be addressed. Indeed, it is known that amine functions can degrade when they are in the ammonium form, according to the retro-Hoffmann reaction, as shown:

$$R - CH_2 - CH_2 - NH_3^+ \rightarrow R - CH{=}CH_2 + NH_3 + H^+$$

This reaction leads to the decomposition of the amino moiety of the compound catalysed by acidic protons. Due to its structure, ADBTMS cannot undergo the retro-Hoffmann reaction. Indeed, as opposed to ATES, this compound has no hydrogen atom in the alpha position of the carbon bearing the amino group. It has to be noted that in the sealed tube ageing method, due to the air confinement, the medium inside the tube is rather acidic. Thus, part of the amino groups is present in the form of ammonium groups.

Considering the results of the ageing in the NO_2 atmosphere, the comparison of the behaviour of the two aminosilane compounds suggests that during this ageing procedure, degradation occurred, at least partly, via an oxidation reaction. The results quoted in Table 2 can be interpreted as showing that under hydrolytic-led degradation (heat/humid ageing), the stability of ATES and ADBTMS was fair, whereas when the degradation involved an oxidation step, the behaviour of both the products similarly led to a small decrease in AR.

3.3. Study of the mechanical properties of the treated papers after ageing

The tensile resistance was studied by comparing treated and untreated papers. In a first approach, only the papers which underwent sealed tube ageing were studied. The results are shown in Table 3. It is clear that the treatment by ATES induced a significant increase in the tensile breaking resistance. This confirms previous results [17]. Both treated and untreated

Table 3
Tensile breaking resistance behaviour of paper STEP2 treated with ATES unaged and aged (90 °C, 14 days in sealed vessel)

	Unaged		Aged	
	Untreated	ATES	Untreated	ATES
BL[a] (m)	2600	3400	2600	3400
Elongation at breaking (%)	2.2	1.9	2.0	1.8
TEA[b] index (mJ/g)	416	449	376	434

[a] BL: breaking length.
[b] Tensile energy absorption.

papers showed a good resistance to ageing. The paper being non-acidic, the mechanical properties imparted by the ATES treatment were maintained during the ageing. It can be seen that due to the increase in the modulus of the material, the elongation at breaking diminished. However, the treatment by ATES provided an increase in the tensile energy absorption (TEA) index, which is in agreement with the strengthening effect brought by the interpenetrated polymer network [20].

As mentioned earlier, the main drawback of the various deacidification processes currently in use worldwide is that they do not impart significantly improved mechanical properties to the treated materials [17,21]. Since in the libraries some of the time-acidified items are so brittle that their handling becomes difficult, a definite asset of a deacidification process would be to significantly improve the mechanical resistance.

It is clear from Table 4 that the ageing in sealed tubes did not significantly modify the folding properties of the paper (34 double folds versus 32). This result is in agreement with previous observations which showed that after ageing, paper STEP2 exhibited approximately the same tensile breaking resistance than before ageing, as measured with the tensile breaking resistance index [3].

After treatment with ATES, it can be seen that the folding endurance (FE) increased for the unaged samples (32 double folds versus 93), as well as for the aged samples (55–64 double folds versus 34). This shows that the incorporation of ATES in the cellulosic web significantly improved the folding endurance, before as well as after ageing. The results also showed that this improvement was effective regardless of the ageing method used, whether mostly hydrolytic or involving an oxidative step. This observation is in agreement with the

Table 4
Folding endurance (FE) (0.5 kg) of paper STEP2 at various states of treatment and ageing (number of folds)

	Unaged	Aged	Type of ageing
Untreated	32[a]	59	80 °C/65% rH
		34	Sealed tube 90 °C
ATES	93	56	NO_2 – 25 °C/50% rH
		55	80 °C/65% rH
		64	Sealed tube 90 °C
ADBTMS	98	143	NO_2 – 25 °C/50% rH
		200	80 °C/65% rH
		252	Sealed tube 90 °C

[a] Average value, measurements carried out by two different laboratories.

Table 5
Tensile properties of paper of book K treated by ATMS unaged and aged (80 °C/65% rH)

		Tensile breaking strength (BL,[a] MD[b]) (m)	Elongation at breaking (%)	Folding endurance (number of folds)
Untreated	Unaged	3700	1.1	176
Untreated	Aged	3300	0.8	74
ATMS/ethanol (10% w/w)	Unaged	5300	1.1	64
ATMS/ethanol (10% w/w)	Aged	4900	1.0	100

[a] BL: breaking length.
[b] MD: machine direction.

results presented in Table 3, which showed that the tensile energy index increased after treatment and ageing. This effect is not thought to be due to the high temperature which would promote the development in the fibre network of a macromolecular network due to silanol condensation. Indeed the pollution ageing was carried out at 25 °C.

The same type of observation can be effected with ADBTMS: for the unaged samples the treatment led to a substantial improvement of the folding endurance (98 double folds versus 32). The surprise came from the observation of the aged samples, where regardless of the method used, FE was significantly improved after ageing compared to before ageing. It can be assumed that a chemical reaction between the aminosilane and the cellulosic substrate is favoured by the ageing procedure. In previous studies, it was shown that paper STEP2 had the same FE before and after thermal ageing [3]. However, the authors found that the exposure to an oxidative ageing process (pollution) induced an important decrease in the tensile resistance, which they correlated to a decrease in the zero span breaking resistance. Conversely, in the present work, after the oxidative-led pollution ageing, the folding endurance of the treated paper was better than that of the untreated paper. From the results obtained here, it can be seen that the treatment with aminosilane compounds provided a good folding endurance to the paper, and that the beneficial effect of the presence of a macromolecular aminosilane network superimposed to the cellulosic network helped overcome the potential effect of the degradation of the paper.

Table 6
M_r averages and polydispersity (PD) index of STEP2 paper: reference unaged (Ref UA) and reference aged (Ref A) and aminosilane treated unaged (ATES UA, ADBTMS UA) and aged (ATES A, ADBTMS A)

STEP2	Avg $M_n \times 10^{-5}$ g mol^{-1}	Avg $M_w \times 10^{-5}$ g mol^{-1}	Avg $M_z \times 10^{-5}$ g mol^{-1}	Avg PD (M_w/M_n)
(1) Ref UA	2.67	4.56	6.85	1.71
(2) Ref A	1.85	3.76	6.44	2.04
(3) ATES UA	2.72	5.72	9.90	2.10
(4) ATES A	2.47	5.33	9.41	2.16
(5) ADBTMS UA	2.51	5.08	8.50	2.03
(6) ADBTMS A	2.78	5.39	8.95	1.94

Table 7
Percent difference in M_r averages between unaged and aged, untreated and treated samples (numbers refer to numbered samples in Table 6)

STEP2	ΔM_n %	ΔM_w %	ΔM_z %
(1) – (2)	30.9	17.4	6.0
(3) – (1)	1.8	20.4	30.8
(3) – (4)	9.3	6.8	5.0
(4) – (2)	25.2	29.5	31.6
(5) – (1)	−6.0	10.4	19.4
(5) – (6)	9.7	5.7	4.9
(6) – (2)	33.6	30.2	28.0

Since paper STEP2 is not acidic, in order to better represent real situations, it was decided to investigate the ageing behaviour of an acidic paper from a naturally aged book (named book K) when treated with the same aminosilane compounds. The results are shown in Table 5. It can be seen that the ATMS treatment gave very good tensile resistance results. This positive effect was maintained after the ageing for 28 days at 80 °C and 65% rH. It can also be noticed that the folding endurance which decreased after the ATMS treatment was partly restored during the ageing. This phenomenon is similar to that observed on the non-acidic paper STEP2, although less pronounced. It has been previously shown that for highly acidic items, the treatment increased the tensile breaking resistance, but that no improvement of the folding endurance was observed [17]. The improvement of the folding endurance thus most likely depends on the initial acidity of the paper. This effect is not yet completely understood, and is under investigation by the authors.

3.4. M_r and MMD characterisation of STEP2 treated with aminosilanes and behaviour during accelerated ageing

Table 6 summarises the values of the average molar masses (M_r) obtained for the paper STEP2 before and after heat/humid ageing (80 °C, 65% rH), both untreated (reference) and treated. The two treatments under investigation in this characterisation phase were ATES and ADBTMS. STEP2 cellulose from the reference showed a fairly high average M_r ($M_w = 4.56 \times 10^5$ g mol^{-1}) with a low polydispersity (PD = 1.71), which is typical of cotton cellulose. Acid hydrolysis of cellulose occurred during the ageing, with a M_w after ageing of 3.76×10^5 g mol^{-1} (17.4% decrease compared to the unaged reference). This result comforted that the time span of the ageing was adapted for that particular paper as it allowed to observe measurable and significant changes of M_r. The MMD was also affected during the ageing: as can be seen from Table 7, the depolymerisation did not proceed homogeneously over the whole molar mass range. The average decrease was proportionally larger in the low-M_r (30.9% loss in M_n) than in the high-M_r (17.4% loss in M_w and 6% loss in M_z). This effect of the heat/humid ageing on the MMD confirmed previous data obtained with 100% cellulose paper (Whatman no.1) [18,19], though it appeared far more pronounced with STEP2 paper.

Both aminosilane treatments had a large impact on STEP2 paper by increasing significantly the average M_r values. Figs. 1 and 2 show the overlaid differential molar mass graphs of the samples treated with ATES and ADBTMS, respectively. The incorporation of ATES in the fibres induced an increase in M_w of the unaged sample by 20.4%. This increase was more pronounced in the high-M_r range (+30.8% in M_z) than in the low-M_r range (+1.8% in M_n). After ageing the average M_r values of the ATES treated sample remained almost unchanged when compared with the unaged treated counterpart (under 10% loss in the M_r averages). The protection effect of the aminosilane imparted to cellulose against acid hydrolysis was especially well illustrated by the values of the average M_r after the ageing process, with a difference of 29.5% in M_w between the ATES treated sample and the untreated one.

The ADBTMS treatment resulted overall in a similar effect on the cellulose of STEP2 as the ATES treatment, with an increase of 10.4% in M_w for the unaged sample, and

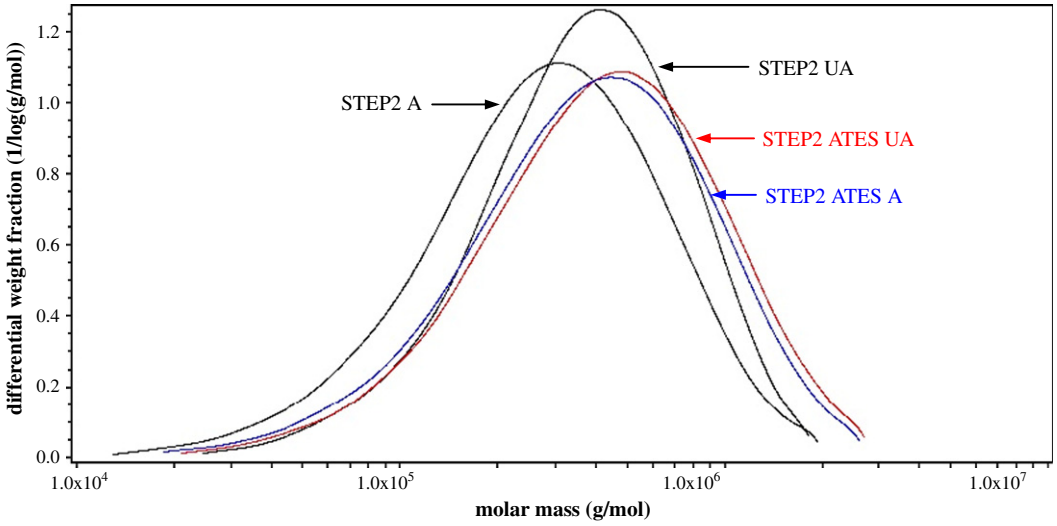

Fig. 1. Overlaid differential molar mass graphs of STEP2 reference unaged (STEP2 UA) and aged (STEP2 A), and ATES treated unaged (ATES UA) and aged (ATES A) samples.

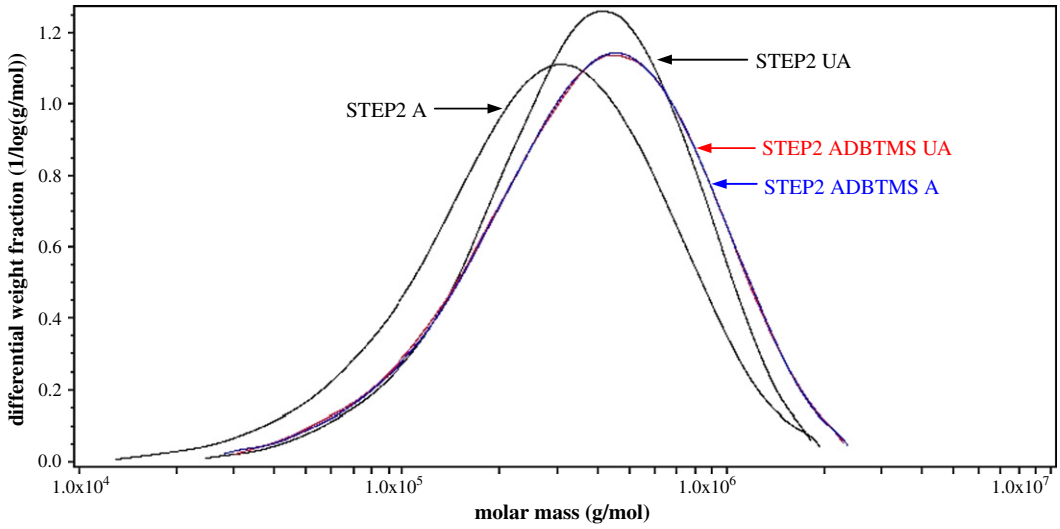

Fig. 2. Overlaid differential molar mass graphs of STEP2 reference unaged (STEP2 UA) and aged (STEP2 A), and ADBTMS treated unaged (ADBTMS UA) and aged (ADBTMS A) samples (note that the curves for STEP2 ADBTMS UA and STEP2 ADBTMS A are superimposed).

a stabilisation of the M_r during ageing (also under 10% loss in all M_r averages), showing again an efficient protection against acid hydrolysis. The difference in M_w between the ADBTMS treated sample and the untreated sample was 30.2%.

4. Conclusion

The treatment by ADBTMS brought a very interesting outcome in that not only the treated paper exhibited higher folding endurance after ageing compared to its untreated aged counterpart, but also generally, compared to the unaged stage, it led to the largest improvement in the mechanical properties upon ageing. The macromolecular characterisation (molar mass determination) showed an effective impact of aminosilanes (ADBTMS and ATES) in stabilising the average molar mass of cellulose during the accelerated ageing, which supported the results at the macroscopic level obtained with the physical testing. The reason for this effect is not yet well established. As demonstrated above, it cannot be attributed only to the resistance to degradation of ADBTMS, since improvement was also observed on the ATMS treated old book acidic paper. Indeed, the simplest hypothesis for this effect is to suppose that when the material containing ATMS or ADBTMS is heated during the ageing, the primary amino groups of the aminosilanes can form a network firmly bound to the fibre surface through a reaction of the amino group with the cellulose chain ends or with the carbonyl groups produced by oxidation. Based on current knowledge, one can assume that this effect would also be observed at room temperature, upon long-term storage. This hypothesis needs further investigation, and if confirmed experimentally, will represent a very promising perspective for mass treatment of paper. For the first time ever a deacidification treatment, besides depositing a sufficient alkaline reserve, would also bring both immediate improvement of the mechanical properties of the treated material as well as continuous improvement upon long-term storage. The application of this effect to room temperature storage can be expected, but the investigation needs carrying out experiments at various temperatures and calculating activation energies for the whole processes. This research will be pursued in order to fully elucidate the mechanism explaining the strengthening effect.

Finally, and not the least, it is worth mentioning that the chemistry of polycondensation between silanol groups involved in this paper treatment process is "green chemistry" which can be used without damage for the cellulosic substrate and which involves chemical products that are safe for the user.

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