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Uptake of Air Pollutants by Paper*

by ANNA JOHANSSON, PETTER KOLSETH & OLIVER LINDQVIST

INTRODUCTION

The effects of environmental pollution on the ageing stability of archival materials have been addressed in several investigations[1–9]. The studies have been focused mainly on the interaction between paper and sulfur dioxide, since this pollutant has been predominant from a historical point of view, due to the combustion of sulfur-containing fossil fuels. The impact of nitrogen oxides and ozone on the degradation processes has attracted less interest in the field of paper conservation.

It is suggested that SO_2 adsorbed in papers is held in two ways, either reversibly or irreversibly. SO_2 is physically adsorbed on the paper surface, dissolved in available moisture in the paper structure and eventually converted into sulfite S(IV):

$$SO_2 + H_2O \leftrightarrow SO_3^{2-} + 2H^+ \qquad (1)$$

The sulfite is reversibly bound to the surface and can readily be desorbed as gaseous SO_2. However, four-valent sulfur is not thermodynamically stable but is known to oxidise to form sulfate S(VI):

$$2\ SO_3^{2-} + O_2 \rightarrow 2\ SO_4^{2-} \qquad (2)$$

This transformation into sulfate is irreversible, and SO_2 cannot then be desorbed from the paper. Damage to the paper is probably related to this chemical change. Studies on several materials exposed to SO_2 have demonstrated the role of NO_x and ozone as catalysts and/or oxidants for the oxidation of S(IV) to S(VI)[10–12] and it may be expected that similar processes are important in paper degradation.

NO_x is produced from reactions between N_2 and O_2 in air during high temperature combustion processes. Automotive exhaust is one of the main sources.

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The only man-made source of O_3 is in reactions involving NO/NO_2. European NO_x emission has increased from rather low values one hundred years ago to the present value. Since 1940 the atmospheric emission of NO_x has increased markedly relative to that of SO_2, and this stresses the increasing importance of NO_x emission. There is often a similarity between indoor and outdoor variations for the pollutants even though the concentration of the pollutants are considerably lower indoors. Both NO_2 and O_3 often occur at higher concentrations than SO_2[13,14].

As already mentioned, SO_2 is by far the most studied air pollutant with regard to the exposure of paper. It was early shown that the edges of books contained more sulfuric acid than the middle areas of the pages[5,15,16]. Old books from the 17th and 18th centuries stored in a highly polluted area were more acid than books of the same edition stored in a rural environment[17]. It is probable that the higher acidity in these books is an effect of air pollution.

A number of investigations have been carried out in which the uptake of SO_2 by paper has been measured. Lyth Hudson and Milner[9] investigated the sulfur uptake on different types of pulp fibres during exposure to 0,5% SO_2 for different times. In general, pulps with low contents of lignin and hemicellulose have a lower uptake of sulfur. Edwards et al.[18] found that relative humidity affects the initial uptake of SO_2 (<48 hours). Initially, a higher relative humidity leads to a greater SO_2 uptake, but after 48 hours the SO_2 uptake is independent of the moisture content. The rate of pick-up of SO_2 is apparently proportional to the square root of the partial pressure of the gas. Atherton et al.[19] concluded that transition metal ions may catalyse the oxidation of sulfur dioxide, thereby increasing its uptake rate.

Recent studies have focused on the influence of NO_2, alone or in combination with SO_2. Daniel et al.[20] and Palm[21] studied the ageing of deacidified paper exposed to $SO_2 + NO_2$. They showed that it is difficult to draw conclusions regarding ageing due to air pollution using data related to mechanical properties of paper. Iversen and Kolar[22] measured the mechanical and optical properties of different types of paper after exposure to NO_2. They found that acid-sized chemical pulp paper deteriorated quickly but that neutral-sized rag and chemical pulp papers containing $CaCO_3$ showed no loss of mechanical strength.

Most studies in the effects of air pollutants on paper have used concentrations of the pollutants ranging from 10 ppm to 0,5%, i.e. considerably higher concentrations than those found even in a heavily polluted urban atmosphere. The degradation of paper due to hydrolysis of cellulose is a slow and temperature-dependent process. It is therefore not easy to detect any changes in mechanical properties as a result of exposure to air pollution at sub-ppm levels. Investigations in high concentrations of pollutants yield rapid results, but there may be

additional effects which lead to ambiguities in interpretation. One problem noted by Williams and Grosjean is that in air at ambient humidity, and with a high SO_2 concentration, sulfuric acid aerosol may be formed and the damage observed on paper may be due to uptake of H_2SO_4 rather than SO_2[23]. They investigated the nature and yields of the reaction products from the exposure of untreated and deacidified paper to ambient levels of SO_2 and NO_2. The study of reaction products is clearly an important way of gaining information about potentially aggressive atmospheric pollutants but there is little to be learned from such studies about the parameters that govern the adsorption of the pollutants on paper.

We have chosen in our study to investigate the first stage in paper deterioration, i.e. the initial dry deposition of pollutants onto a paper surface. Dry deposition includes the deposition of the pollutant in a gaseous form as well as in a particle form. This is probably the dominating route for the deposition of pollutants in an indoor environment. The rate of deposition depends on several factors, including the composition of the paper, and environmental parameters such as relative humidity, the mixture of pollutants, temperature etc.

We have investigated the dependence on humidity and SO_2-concentration, and the influence of NO_2 and O_3 on the SO_2 deposition on different paper grades. The rates of deposition of NO_2 and O_3 on the papers were also studied. The concentration levels used were those of ambient conditions in a moderately to heavily polluted environment[24]. The depositions of NO_2 and O_3 were judged to be insignificant in the present study. The deposition of SO_2 was however, enhanced by the presence of these pollutants, and also by a high relative humidity. The total uptake of air pollutants in the paper samples was so low that no deterioration in paper properties, such as strength, could be detected.

EXPERIMENTAL

Deposition test equipment

The experiments were carried out using time-resolved analysis of the deposition (TRAD) of SO_2, NO_2 and O_3. The equipment was designed specially for deposition studies. The main advantages of the equipment were the high accuracy in the control and regulation of temperature, gas flow, relative humidity and concentrations of gaseous pollutants such as SO_2 and NO_2. The apparatus was made entirely of glass and Teflon[25].

The system was immersed in a thermostated water tank. The polluted atmosphere was created by allowing purified and dried air to enter through two

different channels. One part was saturated with water vapour at the exposure temperature (22°C). The temperature in the laboratory was kept above the temperature in the water tank in order to avoid water condensation at the humidifier. The other part was used as a carrier for the pollutants. SO_2 and NO_2 were added from permeation tubes which contained the pollutants in liquid form. The concentration of the gaseous pollutants was controlled to within 2 ppb. O_3 was produced by allowing dry air to flow past an adjustable ozone generator that uses UV radiation to form atomic oxygen from molecular oxygen which then reacts with undissociated oxygen molecules to form O_3. The O_3 concentration was held to within ±5% of the desired concentration. The relative humidity was adjusted within an accuracy of ±0,3% by mixing measured amounts of dry and humidified air.

The gas flows were then mixed and thermostated and the resulting gas was passed through the exposure chamber. The tubular exposure cell had an inner diameter of 48 mm. The gas flow through the cell was 1,00 dm^3/min, resulting in a laminar flow speed of 0,9 cm/s in the cell (Reynold's number = 12). The paper test piece was suspended by a nylon string in the middle of the chamber so that the direction of flow was parallel to the test piece.

The gas emanating from the exposure chamber was analysed continuously. SO_2 was determined using a fluorescence instrument (Environnement AF21M) which had a sensitivity of 0,001 ppm and a time constant of one minute. NO_2 was determined with a chemiluminescence instrument (Environnement AC230M) which had a sensitivity of 0,002 ppm and a time constant of one minute. O_3 was monitored with a UV photometric O_3 analyser (Dasibi 1108) with a detection limit of 1 ppb. Instrument calibrations involved the use of permeation tubes for SO_2 and NO_2. The concentrations of SO_2 and NO_2 were calculated from the weight loss of the permeation tube and from the flow rate. The deposition of air pollutants was calculated from the difference in concentration between inlet and outlet.

Before the start of the experiment, the interaction of the pollutants with the chamber walls had reached a steady state, and the effect of the absorption of pollutants by the apparatus could therefore be disregarded.

Paper samples used in the study

Five commercially available papers, four copy papers and one archive paper, were chosen to represent different paper grades:

A Acid lignin-free copy paper: Bleached kraft pulp (SW* 40%, HW** 60%), 18% kaolin, rosin sized.

B Alkaline lignin-free copy paper: Bleached sulfite pulp (SW* 60%, HW** 40%), 18–20% $CaCO_3$ (chalk), neutral sized.

C Acid lignin-containing copy paper: Groundwood pulp (SW* 35%), bleached chemical pulp (SW** 30%, HW** 35%), rosin sized.

D Alkaline lignin-containing copy paper: Groundwood pulp (SW* 52%), bleached CTMP*** (aspen 26%), bleached chemical pulp (SW* 20%, HW** 2%), 2–3% $CaCO_3$, neutral sized.

E Archive paper: Bleached cotton (linters and combers), 2–3% $CaCO_3$, 0,5–1% TiO_2, neutral sized.

* SW = softwood, ** HW = hardwood, *** CTMP = chemi-thermomechanical pulp

Paper is a material with a rather high porosity and a high specific surface, and the surface that may be exposed to air pollutants is therefore much larger than the macroscopic sheet surface (Table 1). The table also gives the content of metal ions, that may already have been present in the native fibres, introduced with different papermaking additives, or could emanate from the pulping and papermaking process equipment. These metal ions may play a significant role in the uptake of air pollutants. The equilibrium moisture content in the papers at different RH levels is given in the last three lines of the Table.

Table 1: Characteristics of the papers samples

Paper		A	B	C	D	E
Grammage (g/m2)		80	80	75	75	80
Specific surface (BET*; m2/g)		1,37	0,95		1,53	0,90
Specific surface** (R ≥ 0,1••m; m2/g)		0,95	0,86		1,35	0,87
Metal ions (AAS***; •g/g)	Cu	0,7	3,9		4,6	1,4
	Fe	55,1	91,4		209	13,8
	Mn	1,2	26,5		6,0	4,0
Pore volume** (cm3/g)		0,395	0,416		0,702	0,419
Porosity** (%)		34	34		44	32
Char radius** (R0,50V,••m)		1,63	1,72		2,51	1,57
Equilibrium moisture content (%) at RH	15%	3,00	3,00	3,80	3,30	2,90
	50%	5,40	5,30	6,20	5,40	5,40
	85%	11,30	11,00	13,80	11,60	10,90

* Determined according to the method of Brunauer, Emmet and Teller

** Determined by Mercury Porosimetry

*** Analysis by Atomic Absorbtions Spectrometry

Test piece preparation

All the investigated papers were of A4 size. The paper test pieces for exposure were taken from the centres of the sheets and cut into strips, 3x10 cm. The geometrical exposure area of the test piece was 60 cm^2 as both sides of the paper were exposed to the gas. The weight of the test piece was 0,24 g. Since paper is a quite porous material, the true surface which is "hit" by SO_2 molecules is much greater; we estimate it to be approximately 2.400 cm^2. The test pieces were preconditioned in desiccators containing saturated salt solutions giving the desired humidity for at least five hours prior to exposure. Only one test piece was exposed at one time and the uptake of the gases was recorded continuously. One exposure lasted until a steady state was reached or at least for 20 hours.

Evaluation of data

The deposition rate is defined as the amount of the gaseous pollutant deposited on the test piece surface per unit time per unit mass of exposed sample, and is calculated from the difference between the input and output concentrations of the pollutants. The deposition rate can also be presented as the amount of gas deposited per unit time per unit area.

The deposition rate in all the graphs is given with respect to unit mass of paper. In all the experiments, the resolution of the SO_2 concentration measurement was 1 ppb which in relation to the flow rate and sample weight corresponds to an SO_2 deposition rate of 0,18 $ng \cdot s^{-1} \cdot g^{-1}$. Calculated with respect to sample area, this is 0,72 $pg \cdot s^{-1} \cdot cm^{-2}$. The deposition rate must be considered in relation to the deposition velocity to an ideal absorbing surface. The deposition velocity, v_d, is defined as the deposition per unit area per unit time [26], i.e. the flux of SO_2 to the surface is divided by the concentration of SO_2. The concentration is taken as the mean of the input and output SO_2 concentrations in the cell. The deposition velocity in all experiments was calculated when the deposition rate had reached an apparently steady state.

The flux to the surface may be described as being retarded by an aerodynamic resistance and by a surface resistance. The aerodynamic resistance may be estimated by measuring the deposition velocity to a surface with no surface resistance – an ideal absorber. This mass-transfer-limited deposition rate of SO_2 to the test piece surface, was found to be 3,8 mm/s at 85% RH and 107 ppb SO_2. The ideal absorber was prepared by soaking a paper test piece in 0,1 M NaOH, and then drying it between filter papers before exposure.

RESULTS: DEPOSITION OF SULFUR DIOXIDE

The influence of different parameters on the SO_2 deposition rate was investigated and the results are here presented in the following order:

- Influence of humidity: 15, 50, and 85% RH,
- influence of NO_2 at 50% and 85% RH,
- influence of O_3 at 50% and 85% RH.

The deposition velocity at a steady state deposition rate was calculated when the decrease in the deposition rate was less than 1 ppb in 5 hours. For most runs, a steady state was reached after approximately 20 hours of exposure. Table 2 shows the calculated deposition velocities on papers exposed to 107 ppb SO_2, 350 ppb NO_2 and 230 ppb O_3 at different relative humidities.

Table 2: The deposition velocities of SO_2 after 20 hours, SO_2=107 ppb, NO_2=350 ppb and, O_3=230 ppb.

Atmosphere		Deposition velocity (v_d; mm/s) in paper sample:			
		A	B	D	E
SO_2	15% RH	<0,03	<0,03	0,07	<0,03
	50% RH	<0,03	0,08	0,34	0,14
	85% RH	0,03	0,21	1,17	0,14*
SO_2+NO_2	50% RH	0,03	0,06	0,27	0,13
	70% RH		0,15		
	85% RH	0,11	0,95	1,08	0,39*
SO_2+O_3	50% RH	0,09	0,13	0,7	0,18
	85% RH	0,23	0,68	0,99	0,38*

* after 25 hours

Influence of relative humidity

Fig. 1a shows the SO_2 deposition on papers exposed to 107 ppb SO_2 at 15% RH. At 15% relative humidity, the SO_2 deposition rate was low on all papers. The initial deposition rate was almost the same regardless of paper type. Alkaline CTMP (D) was the only paper which still had a measurable deposition rate of SO_2 when the exposure was interrupted after 20 hours.

At 50% RH, the initial SO_2 deposition rate was higher than at 15% RH on all papers, Fig. 1b. Differences in SO_2 uptake on the papers due to paper quality was noted primarily during the initial stage of exposure. The decrease in deposi-

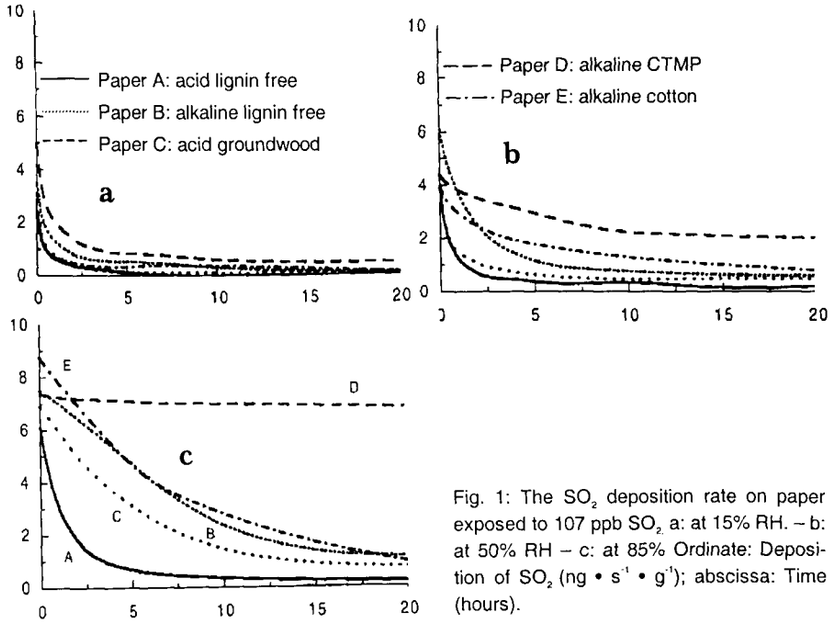

Fig. 1: The SO_2 deposition rate on paper exposed to 107 ppb SO_2. a: at 15% RH. – b: at 50% RH – c: at 85% Ordinate: Deposition of SO_2 (ng • s^{-1} • g^{-1}); abscissa: Time (hours).

tion rate with time was lower on alkaline CTMP (D) and the deposition rate at steady state on this paper was almost five times higher than the rate at 15% RH.

At 85% RH, the uptake of SO_2 was substantially higher on all papers, Fig. 1c. Just as at lower humidities, alkaline CTMP (D) differed from the other paper grades. Instead of a fast rate decline during the first 10 hours of exposure, which was the case for the rest of the paper grades, a steady-state was reached from the start of the exposure on this paper.

The effect of the presence of nitrogen dioxide

The deposition rate curves for SO_2 in the presence of 350 ppb NO_2 at 50% RH, Fig. 2a are similar to those in Fig. 1b, i.e. there was no significant influence of NO_2 on the SO_2 uptake on paper during exposure at 50% RH. At 85% RH, the presence of NO_2 increased the rate of deposition of the SO_2 at steady state for all papers with the exception of the alkaline CTMP (D), Fig.2b. The effect of NO_2 was most pronounced on alkaline lignin-free (B). The decrease in the deposition rate with time on alkaline cotton (E) was much slower than during exposure to

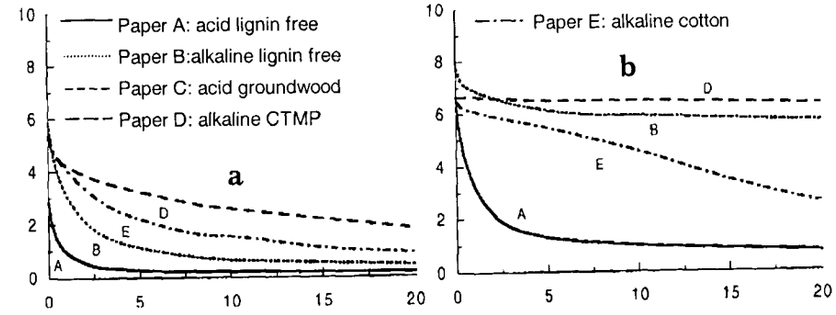

Fig. 2: The SO_2 deposition rate on papers exposed to 107 ppb SO_2 and 350 ppb NO_2; a: at 50% RH – b: at 85% RH. Ordinate: Deposition of SO_2 (ng • s^{-1} • g^{-1}); abscissa: Time (hours).

SO_2 alone; after 20 hours, the deposition rate was almost three times higher. The exposure was continued for five more hours and the rate of deposition of SO_2 did not change during this time, but remained at approximately 2,5 ng·s^{-1}·g^{-1}. A significantly higher SO_2 uptake on acid lignin-free (A) was noted in the presence of NO_2. The initial rate decline was slower than in the corresponding run with SO_2 alone.

Since the synergism between SO_2 and NO_2 was so pronounced on alkaline lignin-free (B) at 85% RH, additional runs at 70% RH were carried out at an SO_2 concentration of 107 ppb. Fig. 3a shows that an increase in humidity from 50% to 70% RH primarily enhanced the initial SO_2 uptake. Results of corresponding runs with the addition of 350 ppb NO_2 are shown in Fig. 3b. The strong synergetic effect of NO_2 at 85% RH was not found at 70% RH.

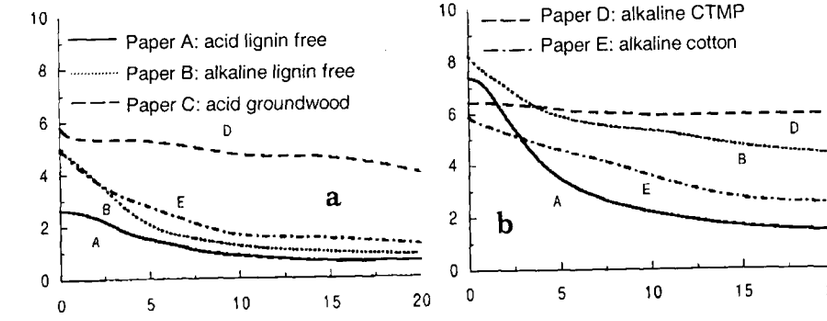

Fig. 3: The SO_2 deposition rate on papers exposed to 107 ppb SO_2 and 230 ppb O_3; a: at 50% RH – b: at 85% RH. Ordinate: Deposition of SO_2 (ng • s^{-1} • g^{-1}); abscissa: Time (hours).

The Effect of the Presence of Ozone

The addition of 230 ppb O_3 accelerated the rate of deposition of SO_2 on all paper grades at 50% RH, Fig. 4a. The SO_2 uptake at steady state was three times higher in the acid lignin-free (A) and twice as high in the alkaline CTMP (D), but was only slightly higher in the alkaline lignin-free (B) and alkaline cotton (E). Fig. 4b shows that the presence of O_3 enhanced the SO_2 deposition rate on all paper grades at 85% RH with the exception of the alkaline CTMP (D). The uptake of SO_2 on acid lignin-free (A) appeared to be more affected by the presence of ozone than on the other paper grades. The uptake of SO_2 on alkaline lignin-free (B) was also considerably greater in the presence of ozone.

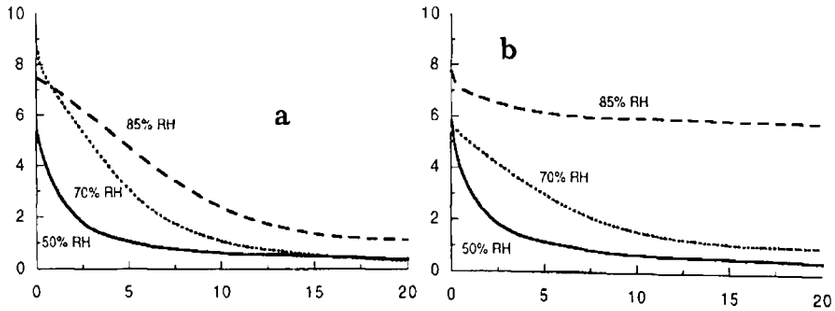

Fig. 4: The SO_2 deposition rate on alkaline lignin-free paper at different relative humidities.a: Exposed to 107 ppb SO_2 ; b: exposed to 107 ppb SO_2 and 350 ppb NO_2. Ordinate: Deposition of SO_2 ($ng \cdot s^{-1} \cdot g^{-1}$); abscissa: Time (hours).

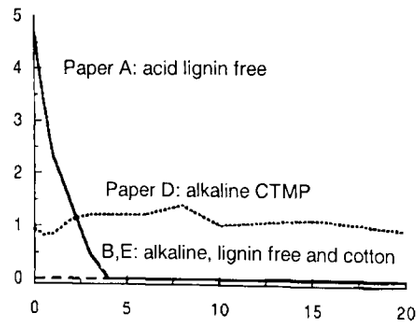

Fig. 5: The NO_2 deposition rate on papers exposed to 350 ppb NO_2 at 85% RH. Ordinate: Deposition of NO_2 ($ng \cdot s^{-1} \cdot g^{-1}$); abscissa: Time (hours).

DEPOSITION OF NITROGEN DIOXIDE ON PAPER

Fig. 5 shows the NO_2 deposition on different paper grades. The papers were exposed to 350 ppb NO_2 at 85% RH. The NO_2 deposition rate was very low, or non-detectable (below the detection limit of 2 ppb), in all the papers. Acid lignin-free (A) picked up a minor amount of NO_2 during the first hours of exposure, but the deposition rate decreased rapidly and, after three hours exposure, no further deposition of NO_2 could be detected. Alkaline CTMP (D) differed from the rest of the paper grades in that a low but invariable NO_2 deposition was recorded on this paper during the 20 hours of exposure.

CONSUMPTION OF OZONE ON PAPER

Fig. 6a shows the rate of consumption of ozone on different papers exposed to 290 ppb O_3 at 50% RH. Ozone consumption was recorded on all the exposed papers during the first 15 hours, but it decreased rapidly. After 20 hours of exposure, it was below the detection limit of the ozone analyser on alkaline lignin-free (B) and alkaline cotton (E) whereas the consumption rate on acid lignin-free (A) and alkaline CTMP (D) had reached a steady state level of approx. 2 $ng \cdot s^{-1} \cdot g^{-1}$.

Fig. 6b shows the ozone consumption on different papers exposed to 230 ppb O_3 at 85% RH. High humidity affected the interaction with alkaline CTMP paper (D) where the ozone consumption was increased three times. The consumption rate at 20 hours on acid lignin-free (A) seemed to be unaffected by the

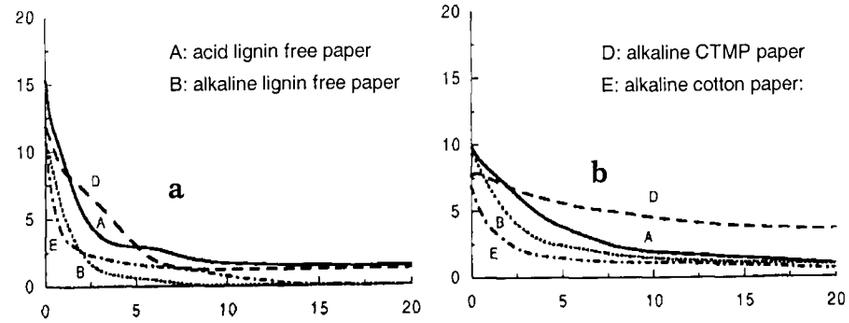

Fig. 6: The ozone consumption rate; a: on papers exposed to 290 ppb ozone at 50% RH. – b: on papers exposed to 230 ppb ozone at 85% RH. Ordinate: Deposition of O_3 ($ng \cdot s^{-1} \cdot g^{-1}$); abscissa: Time (hours).

humidity. A small but significant consumption of O_3 was detected on the alkaline papers, alkaline lignin-free (B) and alkaline cotton (E).

Discussion

The uptake of NO_2 seemed to be insignificant in the present study. At higher concentrations, chemical reactions may of course occur between NO_2 and paper compounds[22], but this was judged to be of minor importance at the concentrations studied in this work. The experimental results indicated that O_3 may react with paper at sub-ppm levels, but at the present time we cannot judge whether this should be attributed to decomposition of O_3 at the paper surface or to direct chemical reaction with the material. The higher ozone consumption on alkaline CTMP could be attributed to reactions with lignin[27,28], – but further experiments are needed if possible reactions between O_3 and paper components are to be clarified. This discussion has therefore focused on the uptake of SO_2, and the effects of relative humidity and the presence of NO_2 and O_3 on this uptake.

The intention of this study has not been to establish meticulous relations between the exact composition of the different paper grades and the uptake of air pollutants. Instead, we concentrate the discussion on the overall differences between the selected papers such as pulp composition and inorganic fillers and from that point of view discuss parameters that potentially govern the uptake of gaseous pollutants in paper.

The influence of relative humidity on the deposition of sulfur dioxide

Humidity primarily influenced the initial SO_2 -deposition (< 15 hours) on paper. This is in agreement with Edwards et al.[18]. The initially enhanced uptake of SO_2 at higher humidity was probably only an effect of the higher moisture content which resulted in more gaseous SO_2 dissolved in a greater amount of adsorbed water. The moisture content at a given RH did not differ greatly between the paper samples (Table 1), and this could not therefore explain the large differences in deposition rates. When an equilibrium between gaseous and adsorbed SO_2 was achieved, the uptake of SO_2 slowed down markedly for all papers. According to Edwards et al. [18], the pick-up of SO_2 is independent of the moisture content after 48 hours. This is in keeping with our results provided that the papers did not contain additives, reactions of which with SO_2 are governed by the presence of water. The influence of humidity on the SO_2 uptake at a steady state is

best illustrated by the two extremes of acid lignin-free and alkaline CTMP, the former being almost resistant to SO_2 at any humidity whereas the deposition rate of SO_2 on the alkaline CTMP was highly humidity dependent. Apart from the different pulp compositions of the two papers, alkaline CTMP contained $CaCO_3$ as filler whereas acid lignin-free contained kaolin.

The uptake of SO_2 on alkaline lignin-free, alkaline cotton and alkaline CTMP was probably related to the calcite content. The reaction mechanisms of SO_2 and calcite have been thoroughly investigated in numerous studies related to accelerated deterioration of cultural buildings, statues etc.[29,30]. Even though the reaction mechanisms for the attack of SO_2 on calcareous stone are far from clarified, it is our belief that similar processes occur in $CaCO_3$ -filled papers.

$CaCO_3$ reacts with SO_2 and forms gypsum which is the thermodynamically stable end product according to:

$$SO_2 + CaCO_3 + \tfrac{1}{2}\,H_2O \leftrightarrow CaSO_3 \cdot \tfrac{1}{2}\,H_2O + CO_2 \qquad (3)$$

$$CaSO_3 \cdot \tfrac{1}{2}\,H_2O \xrightarrow{ox/cat} CaSO_4 \cdot 2H_2O \qquad (4)$$

At room temperature, however, the reaction of SO_2 with $CaCO_3$ is very slow. The reaction rate increases when the adsorbed water layer on the $CaCO_3$ particles increases with relative humidity[31,32]. Since the intermediate reaction product calcium sulfite (eq. 3) forms a fairly stable layer on the surface of calcium carbonate in a humid SO_2 atmosphere, it hinders SO_2 from reacting with the underlying $CaCO_3$ with a decreasing reaction rate of SO_2 as a consequence. In the presence of an oxidiser/catalyst, calcium sulfite is readily oxidised to calcium sulfate (eq. 4), which is less dense than the sulfite and allows passage of SO_2 to the underlying $CaCO_3$.

This may be a possible explanation for the different behaviours of the three alkaline papers which contain calcite as a filler. The high reaction rate of SO_2 on the alkaline CTMP at 85% RH may have been due to the presence of additives with a catalytic effect. Atherton et al.[19] noted that the occurrence of metal ions such as Cu(II) and Mn(II) strongly accelerates the uptake of SO_2 in paper. Investigations by Elfving et al.[33] demonstrated the catalytic sulfation of calcite in the presence of Fe_2O_3 and MnO_2.

A more plausible explanation would be the high mechanical pulp content in combination with the alkaline filler in the alkaline CTMP. It has been shown that SO_2 reacts with lignin in a mechanical pulp[34]. Any acidic products formed should be neutralised by reaction with calcite which also reacts directly with SO_2 according to eqs. (3) and (4).

An increasing deposition rate with increasing humidity was also recorded on acid groundwood, although it was somewhat lower than on alkaline lignin-free

$$SO_2 + O_3 + H_2O \rightarrow SO_4^{2-} + O_2 + 2H^+ \quad (5)$$

The deposition velocity of SO_2 on acid lignin-free was three times higher in the presence of O_3 at 50% relative humidity. The effect was even more dramatic at 85% RH as the deposition rate of SO_2 was seven times higher in the presence of 200 ppb O_3.

The consistently high rate of deposition of SO_2 on alkaline CTMP suggests other reactions besides the sulfation of calcite in this paper, e.g. sulfonation of lignin. The higher rate of deposition of SO_2 in 50% RH in the presence of O_3 supported this suggestion of parallel reactions in paper. A deposition rate after 20 hours comparable to that in the alkaline lignin-free would be expected if the adsorbed SO_2 had reacted solely with calcite.

The reaction of SO_2 with alkaline lignin-free and in some measurements with the alkaline cotton was consistent with what has been demonstrated on sulfation of calcite. The higher SO_2 deposition rate on alkaline lignin-free and alkaline cotton may again be assigned to the presence of calcite. The adsorbed four-valent sulfur on the paper was either oxidized directly to its six-valent state or reacted with water and calcite to form gypsum via calcium sulfite (eqs. 3 and 4). The synergetic effect of ozone is favoured by a higher humidity[32].

These results, especially for acid lignin-free, clearly demonstrate the negative influence of O_3 on the permanence of so-called unprotected papers such as rosin-sized and those containing groundwood. We believe that ozone plays a significant role for the air-pollutant-related deterioration processes of paper. The results indicate the importance of regulating humidity and controlling air pollutants besides SO_2 in the air supply to archives and libraries.

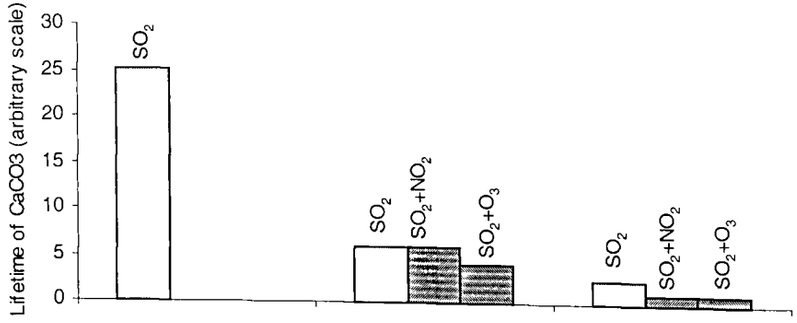

Fig. 7: The estimated lifetime of 15% $CaCO_3$ filler in the alkaline lignin-free copy paper in different polluted environments. The concentrations are: SO_2 = 107 ppb, NO_2 = 350 ppb, O_3 = 230 ppb

The consumption of alkali reserve due to the uptake of sulfur dioxide

It was established early that the presence of $CaCO_3$ favours ageing stability[15]. If a small percentage of $CaCO_3$ is present, paper is regarded as "permanent"[30]. Under controlled conditions, this is probably in agreement with reality. However, one should bear in mind that under severe conditions, the alkalinity of the filler may rapidly be consumed. Fig. 7 presents a rough estimate of the durability of the buffer in alkaline lignin-free paper calculated from the steady-state deposition rate of SO_2 under ambient conditions. This rough estimate describes the relative importance of the relative humidity, NO_2 and O_3 on the uptake of SO_2 in an alkaline paper. However, it should be noted that paper sheets are rarely exposed freely but are stacked in boxes or bound volumes.

CONCLUSIONS

The main conclusions from the present study of how air pollutants are deposited on and attack paper materials may be stated as follows:

- Investigated papers showed slow deposition rates of SO_2 on exposure to SO_2 alone.
- The addition of NO_2 increased the uptake of SO_2 at high relative humidities.
- The addition of O_3 also increased the uptake of SO_2 at intermediate humidities.
- The capacity of an alkaline buffer for neutralising acid pollutants in paper probably depends upon the paper manufacturing process and the origin of the filler.
- The relative humidity in repositories should be kept as low as possible in order to minimise the interaction of air pollutants in paper.

ACKNOWLEDGEMENTS

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and alkaline cotton. As this paper contains approx. 30% mechanical pulp, the higher SO_2 deposition rate compared to that on acid lignin-free can probably be assigned to sulfonation of lignin.

Of the papers investigated, only the kaolin-filled acid lignin-free showed a low deposition rate of SO_2 at all humidities ($v_d < 0{,}03$ mm/s; cf. Table 2) after 20 hours. Kaolin has no buffer capacity towards acidic species and provides no protection of the fibres. The pick-up of SO_2 is therefore to a higher degree related to reactions with cellulose than in the calcite-filled papers. The rate-controlling step is probably the conversion of adsorbed S(IV) to S(VI). Efforts have been made to prove the presence of S(IV) species in paper[23]. Due to the instability of SO_3^{2-} in aqueous medium, wet chemical analysis methods are unfortunately too vigorous and subsequently only SO_4^{2-} has been isolated. It is, however, probable that the deposition rate of SO_2 is related to the oxidation of S(IV) species adsorbed on the fibre. This process is obviously slow in ambient concentrations of SO_2 at room temperature and is independent of humidity.

Since the calcite in alkaline cotton paper probably shields the fibres from reacting with SO_2, we cannot comment upon the stability of cotton cellulose towards dry deposition of SO_2. The uptake of SO_2 on pure cotton cellulose was however studied in a parallel investigation[35]. A similar behaviour was then found for cotton cellulose as for acid lignin-free, i.e. SO_2 at ambient concentrations did not react at any significant rate with cotton cellulose at any of the humidities studied.

The effect of nitrogen dioxide on the deposition of sulfur dioxide

The addition of NO_2 at 50% RH had no effect on the SO_2 deposition on any of the exposed paper grades. The deposition velocities at steady state were unaltered compared to the corresponding runs in an SO_2 environment.

On addition of NO_2 at 85% RH, the rate of SO_2 uptake was significantly enhanced on all papers, except for the alkaline CTMP. Simultaneously with the SO_2 measurements, the NO_2 concentration was monitored. The NO_2 concentration was the same irrespective of whether SO_2 was present or not i.e. there was no NO_2 consumption that corresponded to the increased deposition of SO_2. No detectable NO was formed. The results indicated that NO_2 took part only as a catalyst. If so, this is in agreement with earlier observations on several materials where the catalytic action of NO_2 has been demonstrated[10,11].

The most interesting result in high humidity was achieved on acid lignin-free. A four-fold increase in the deposition velocity of SO_2 in high humidity was noted when NO_2 was added. The increase in the SO_2 deposition rate was probably

due to an increase in the oxidation of adsorbed four-valent sulfur on the surface. The enhancement of oxidation of S(IV) on an "unprotected" paper with no alkali reserve will probably result in an accelerated accumulation of sulfuric acid (eqs. 1 and 2) which then promotes the hydrolysis of cellulose.

The strong synergetic effect on the SO_2 deposition when the alkaline papers were exposed to SO_2 plus NO_2 at high humidity may be explained by the high $CaCO_3$ content. The catalytic effect of NO_2 on the oxidation of four-valent sulfur adsorbed on a calcite surface has been reported by Johansson et al.[10]. The presence of NO_2 promotes the forming of gypsum, $CaSO_4 \cdot 2H_2O$ according to eqs. (3) and (4), and thus allows a greater pick-up rate of SO_2 on the paper. As this strongly synergetic effect was not seen below 85% RH, the presence of water seems to be crucial for the SO_2 / NO_2 interaction on paper.

The addition of NO_2 had no effect on the rate of deposition of SO_2 on alkaline CTMP, indicating that the limiting deposition velocity on this paper was already reached in an environment of SO_2 alone ($v_d = 1{,}1$ mm/s).

Alkaline cotton behaved unexpectedly, as the rate of SO_2 deposition decreased with time in the presence of NO_2 in spite of the excess amount of $CaCO_3$ present. At steady state, the deposition velocity was barely half as high as for the alkaline lignin-free and alkaline CTMP papers. The $CaCO_3$ in both alkaline cotton and alkaline lignin-free originated from chalk, and for that reason we expected the same behaviour in the SO_2 + NO_2 environment for both papers. Whether or not this lower deposition rate compared with that on the alkaline lignin-free is a disadvantage for the ageing stability is a matter of discussion. If it is assumed that all the adsorbed SO_2 reacts with $CaCO_3$, the alkaline filler in alkaline cotton will last longer than that in the other two papers and thus prolong its permanence. However, an alternative explanation of the low deposition rate on the alkaline cotton could be that the calcite particles were partially shielded from reacting with SO_2, for example through the formation of a film of dry-strength resin over their surface.

Since humidity seemed to play a significant role in the SO_2/NO_2 interaction on paper, the higher rate of oxidation of SO_2 due to the presence of NO_2 may be avoided by keeping the humidity as low as possible.

The effect of ozone on the deposition of sulfur dioxide

The uptake of SO_2 by paper was significantly increased by the presence of O_3, Table 2. Ozone is an efficient oxidizing agent and we believe that it accelerated the deposition rate of SO_2 by oxidation of the four-valent sulfur bound to the paper surface according to:

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SUMMARIES

Uptake of Air Pollutants by Paper

The objectives of the study have been to investigate the uptake of air pollutants (SO_2, NO_2 and O_3), especially synergistic effects when these pollutants are present together, and the effects of climate.

The initial dry deposition of the pollutants onto a paper surface was studied using on-line gas analysis. The paper samples were exposed to synthetic atmospheres with careful control of pollutant concentrations, relative humidity and flow conditions.

The depositions of NO_2 and O_3 were judged to be insignificant in the present study. The investigated papers showed a low tendency to pick up SO_2 alone. The deposition of SO_2 was however enhanced by the presence of the other pollutants, and also by a high relative humidity. The addition of NO_2 increased the pick-up of SO_2 at high relative humidities, while the addition of O_3 also increased the pick-up of SO_2 at intermediate humidities.

The presence of $CaCO_3$ favoured a high pick-up of SO_2 on the alkaline papers. However, it was found that the alkaline papers responded differently to SO_2. This may indicate that the alkali reserve under adverse conditions is either too rapidly consumed or passivated, probably due to the paper manufacturing process and the origin of the filler.

Absorption des gaz polluants par le papier

L'objectif poursuivi par cette étude consistait à rechercher comment les gaz polluants (SO_2, NO_2 et O_2) étaient absorbés par le papier. Des recherches ont été effectuées notamment sur les effets synergétiques de ces gaz polluants lorsqu'ils étaient présents en même temps dans l'air environnant. Le dépôt initial, lorsque l'air est sec, des gaz polluants sur la surface du papier a été mesuré selon la méthode de l'on-line gas analysis. Les échantillons de papier ont été exposés à une atmosphère créée artificiellement comportant des concentrations de gaz précisément dosées sous des conditions bien déterminées d'humidité relative et de circulation d'air. Cette étude a permis de considérer que le dépôt de NO_2 et de O_2 a une signification négligeable. Les échantillons de papier étudiés ont démontré une certaine tendance, cependant assez minime à absorber SO_2 lorsque celui-ci est le seul gaz présent dans l'atmosphère. L'absorption de SO_2 se trouve considérablement renforcée par la présence d'autres gaz polluants ainsi que lorsque le taux d'humidité ambiante monte. L'addition de NO_2 entraînait une plus forte absorption de SO_2 lorsque les taux d'humidité relative étaient élevés alors que l'addition de O_2 favorisait l'absorption de SO_2 même à des taux moyens d'humidité relative. La présence de $CaCO_3$ favorisait une forte absorption de SO_2 par les papiers alcalins. On a cependant observé que les papiers alcalins réagissaient différemment à SO_2. Ceci peut signifier que, sous certaines conditions défavorables, soit que la réserve alcaline se consomme trop rapidement, soit qu'elle se désactive, probablement pour des raisons liées au processus de fabrication du papier ou à l'origine de la matière de remplissage.

Die Aufnahme von Gasen der Umweltverschmutzung durch Papier

Das Ziel der Untersuchung, über die berichtet wird, war es festzustellen, wie die Gase SO_2, NO_2 and O_3 von Papier aufgenommen werden, und insbesondere ihre Zusammenwirken, wenn sie nebeneinander in verschmutzter Luft vorkommen.

Der anfängliche, bei Trockenheit stattfindende Niederschlag der Umweltgase auf die Papieroberfläche wurde durch laufende (on line) Analyse dieser Gase ermittelt. Die Papierproben wurden einer künstlich geschaffenen Umluft mit genau eingestellter Gaskonzentration, Feuchtigkeit und Luftbewegung ausgesetzt.

Aufgrund der Untersuchung wurde geschlossen, daß der Niederschlag von NO_2 und O_2 unwesentlich ist. Die untersuchten Papiere zeigen eine gewisse, aber geringe Neigung SO_2 aufzunehmen, wenn es allein in der Umluft vorhanden war. Die Aufnahme von SO_2 wurde jedoch erheblich verstärkt durch das Vorhandensein der anderen Umweltgase und auch durch erhöhte Luftfeuchtigkeit. Der Zusatz von NO_2 erhöhte die Aufnahme von SO_2 bei hoher Luftfeuchtigkeit, während ein Zusatz von O_3 die Aufnahme von SO_2 auch bei mittleren Feuchtigkeiten erhöhte.

Das Vorhandensein von $CaCO_3$ beförderte eine hohe Aufnahme von SO_2 durch das alkalische Papier. Es wurde jedoch festgestellt, daß alkalische Papiere sich gegenüber SO_2 verschiedenartig verhalten. Das mag ein Zeichen dafür sein, daß entweder die alkalische Reserve unter ungünstigen Bedingungen zu rasch verbraucht oder inaktiviert wird, möglicherweise als Folge des Herstellungsprozesses oder bedingt durch die Herkunft des Füllstoffs.

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Changes in Some Properties of Aged and Historical Parchment

by GOMAA ABDEL-MAKSOUD & EWA MARCINKOWSKA

INTRODUCTION

The use of parchment dates back to the Middle Kingdom in Egypt[1,2]. In spite of the ability of modern technology to preserve information in the form of microfilm, there are many instances where old parchment records are still recognized as certified and trusted documents[3].

Conservators have long been concerned about the damage caused by exposure to temperature in display and storage conditions. Because of natural ageing, historical parchment is likely to be warped and buckled, to have disintegrated, to have become hard, brittle and stained, and also to have been exposed active microbiological attack. The factors provoking natural ageing of parchment are: its reaction to both atmospheric moisture and water, and the effect of heat; this last probably being the major factor in the deterioration of a large portion of native untanned skin (i.e. parchment) in museum collections[4].

There is no doubt that the first stage of any conservation process should always be a detailed study of the condition of the object, with an understanding of deterioration processes, in order to establish a conservation treatment. This study on parchment, therefore, aims to examine the effect of heat as an individual factor of deterioration by comparing the changes in properties of artificially heat aged parchment with those of historical samples.

In Egypt, there are many parchment manuscripts at different sites (museums, stores, libraries and excavation areas). Many of these sites, especially museums and stores, are old and rarely built with a controlled environment. Changing humidity, high temperature, excessive light, air pollution, or a combination of these factors have caused the deterioration of these parchment objects.

EXPERIMENTAL SAMPLES

New samples

Modern parchment from goat was prepared by Abdel-Maksoud[5] acording to Reed[6] and Abdel-Hamid[7].

Historical samples

- Library of the Medical Faculty, Cairo University. Most of them date back to the time of Kolut Pek (19th century) and to the time of Ali Basha Ibrahium (20th century). The studied samples were taken from a parchment certificate.
- Tanta Excavation. Three parchment manuscripts in Hebrew, presenting the Pentateuch of the Old Testament 18th and 19th, centuries. Jewish cemetery, Tanta city, Egypt.
- The Coptic Museum. This museum contains a library for parchment manuscripts. Some samples were taken from this library; written in black ink, most of them date back to the Coptic period in Egypt (5th and 6th centuries).

ACCELERATED AGEING

Heat treatment was used in the accelerated ageing process according to Larsen[8] and Chahine[9] at 70°C, 100°C and 134°C. The period of ageing was between one and four weeks.

SHRINKAGE

Generally, one property of collagen fibres is that they exhibit a sudden shrinkage when heated. The shrinkage temperature of limed collagen ranges from 50°C to 60°C[10]. Degraded collagen fibres have a lower shrinkage temperature[11–13]. To prove this the shrinkage temperature was measured by using the micro-hot table technique and a polarizing microscope.

Preparation for shrinkage temperature measurement

Haines[14] noted that shrinkage temperature should be measured under controlled conditions, which include the need for the parchment samples to be thoroughly

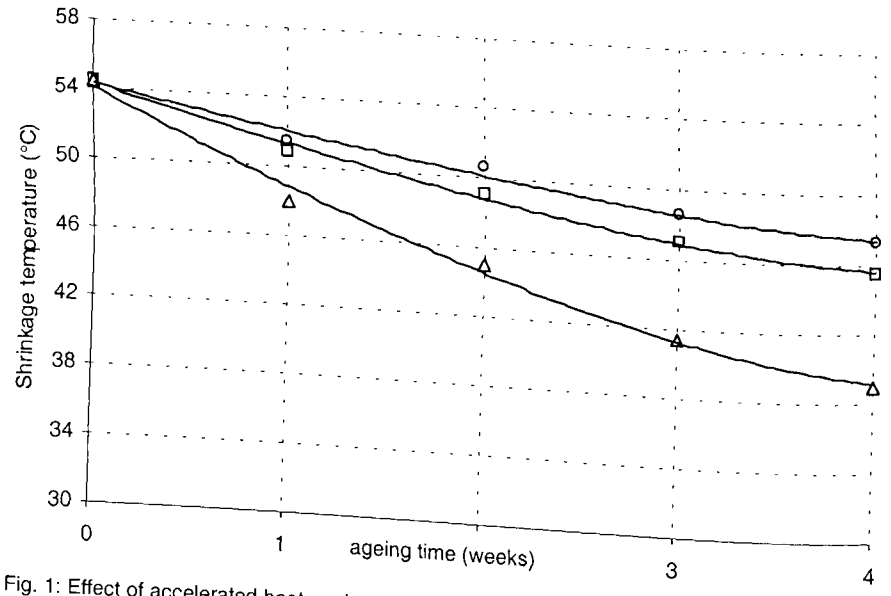

Fig. 1: Effect of accelerated heat ageing at different temperatures on the shrinkage temperature of modern parchment. ○ 70°C – □ 100°C – Δ 134°C.

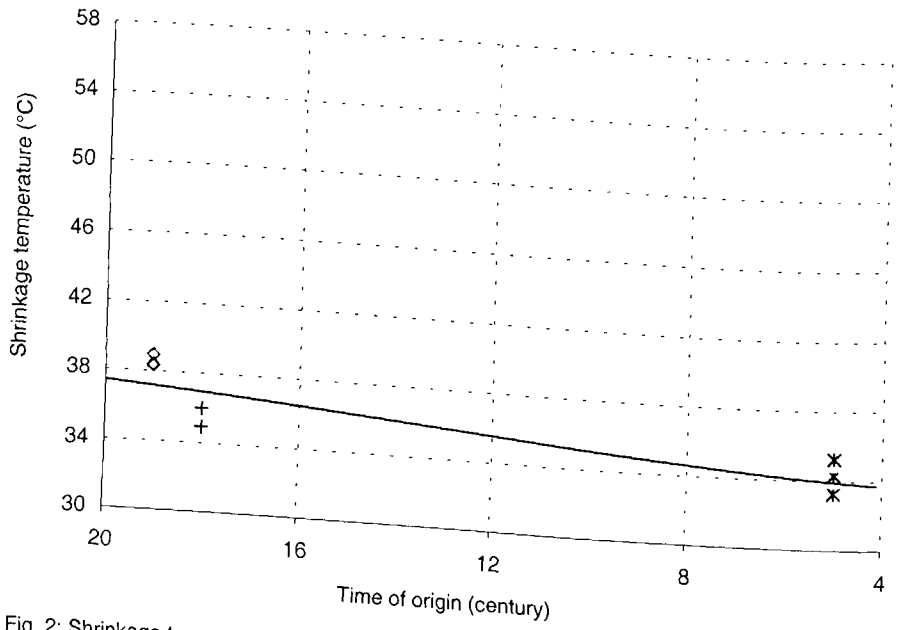

Fig. 2: Shrinkage temperature of historical parchment of different age: ◊ Samples of the Medical Library – + Samples of Tanta Excavation – ✱Samples of the Coptic Museum.

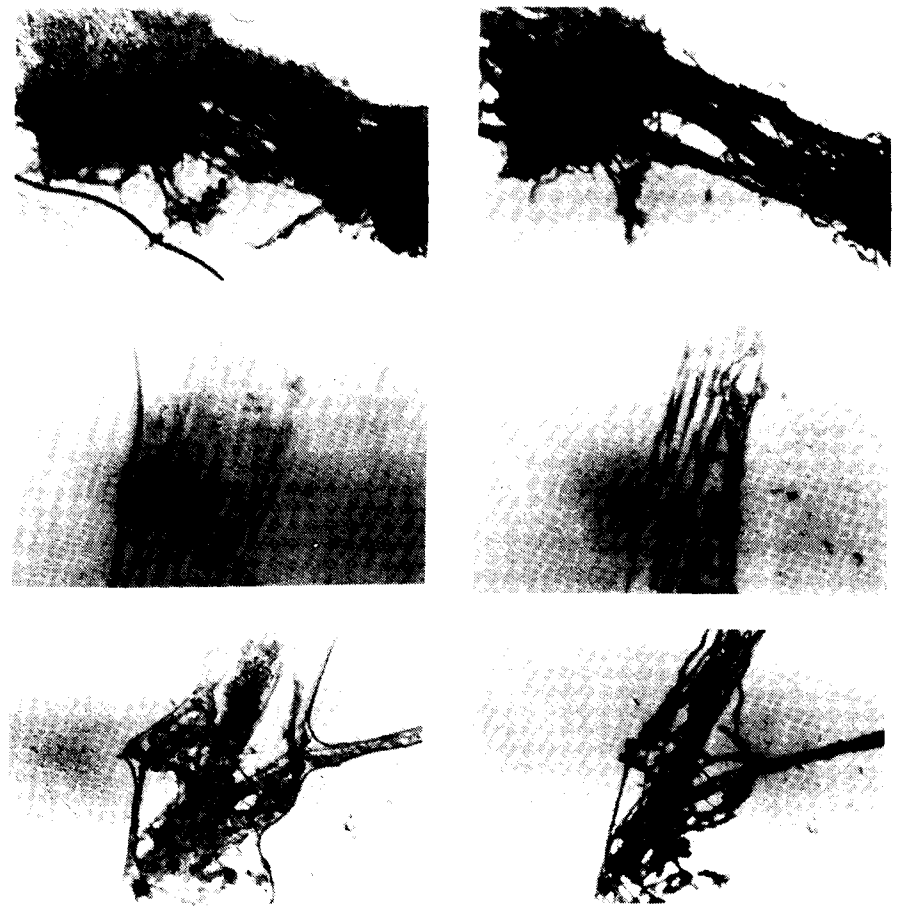

Fig. 3: Microscopical pictures of modern parchment after accelerated ageing at room temperature (left column) and at shrinkage temperature (right column). 1,2: ageing at 70° C; 3,4: ageing at 100°C; 5,6: ageing at 134°C.

RESULTS

Generally, parchment appears to tolerate temperatures of 130°C for periods of at least a few weeks. At higher temperatures modern parchment begins to curl at the edges and becomes slightly darker in colour. Reed[6] reported that all parchment at a temperature range of between 130°C–150°C, generally shrinks in all dimensions and curls into a roll which, on removal from the oven, is extremely hard and brittle and proves to be impossible of being reconditioned to its former state.

wet in distilled water. This was achieved by using several changes of distilled water. It was felt that the changes of water would help to lessen any contamination, by salts for instance, influencing the pH. The samples were heated at a rate of 3°C per minute.

Measurement of shrinkage temperature

The procedure, according to Young[15], for measuring the shrinkage temperature using the hot stage was followed. Once cut, the fibers, positioned between glass depression slides, were degreased in acetone for five minutes and then soaked in distilled water for approximately five to ten minutes. After this procedure they were transferred using steel tweezers to a second bath of distilled water for a minimum of 45 minutes to allow full saturation. moved to a microscope slide prepared with a small reservoir of distilled water containing glycerine, which kept the fibers continually hydrated and unrestrained throughout the heating cycle. Each transfer, from acetone to water and water to slide, was performed quickly to ensure that the fibers did not dry out, as this would falsely lower the shrinkage temperature. The slide containing the fibers was inserted into the hot stage, which was placed onto the stage of the polarizing microscope. The shrinkage process was observed at magnification factor 100 using a polarizing light microscope.

Once the hot stage was activated and the shrinkage temperature range of the sample was reached the structural order within the fibers became disrupted. The fiber shrank and lost birefringence. This shrinkage and loss of birefringence continued as the temperature increased.

Measurements were performed on modern parchment after weeks 1, 2, 3 and 4 of heat ageing. Additionally, measurements were made on the historical samples.

MECHANICAL PROPERTIES

Mechanical properties were measured according to ISO 3376[16]. Samples were taken from adjacent zones of a skin. These samples were 90 mm long, the free length between jaws of the testing machine was 50 mm, and the width of the free length was 10 mm. The average thickness of the new samples was 0.33 mm ± 0.02 mm. The average thickness of the historical samples was 0.43 mm ± 0.03 mm. Six samples were taken from the modern skins, three perpendicular to and three parallel to the backbone, and the three results averaged for each direction. Only

one sample could be taken from the historical parchments. The speed of stretching during measuring was 100 ± 20 mm/min. A Universal Testing Machine (Model 1435, producer: Zwick (Ulm, Germany) was used for measuring. The samples were measured after conditioning for 48 hours at 20°C and 65 % RH according to ISO 554[17]. The tensile strength is found by dividing the breaking force (N) by the product of width and thickness of the samples (mm). The results are expressed as N per mm^2. The elongation at break is given in %.

HUMIDITY SORPTION

Determination of moisture content was based on the weight loss of a sample dried by the action of infrared heating rays directed on the sample (heating from within), using a Mettler LP16 Infrared Dryer. The instrument is mounted on a precision balance, which is connected to a computer and printer so that complete records of the drying profiles and the final results can be produced. The temperature during this process is 105°C. Water molecules strongly absorb infrared radiation, which result in the rapid evaporation of the water. Before the procedure of drying, the samples were placed for five days in top of a desiccator, which was filled with saturated solution of di-sodium hydrogen orthophosphate ($Na_2HPO_4 \cdot 12\ H_2O$) to create a relative humidity of 95%. The temperature was 20°C.

CHANGE OF COLOUR

Colour changes caused by heat were measured using the CIE*Lab system, commonly used to compare the colours of two samples. The L scale measures lightness, and varies from 0 (black) to 100 (perfect white). The a-scale measures red-green; +a means *more red*, -a means *more green*. The b-scale measures yellow-blue, +b meaning *more yellow*, -b *more blue*. Differences in colour between two specimens are determined by the use of the Greek letter Delta (ΔL, Δa, Δb); the total colour difference (ΔE) is found according to the following equation[18]:

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}$$

The measurement was made using a Shimadzu Double Beam UV-2101 PC Spectrophotometer equipped with ISR 48 Integrating Sphere.

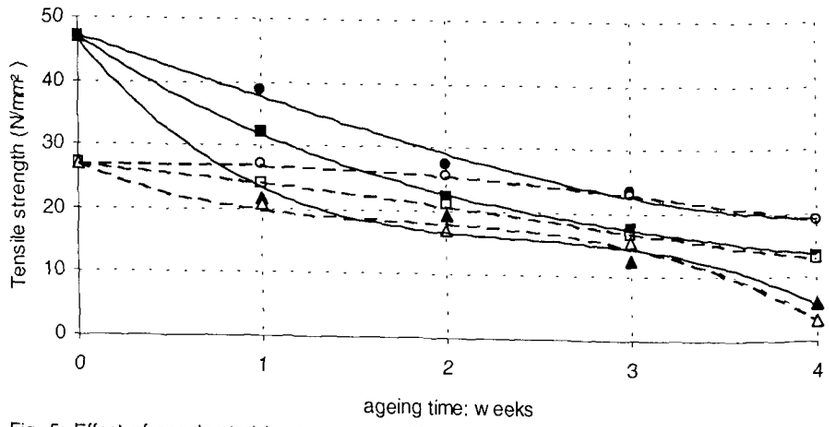

Fig. 5: Effect of accelerated heat ageing at different temperatures on the tensile strength of modern parchment.

○ ● ageing at 70°C – □ ■ ageing at 100°C – Δ ▲ ageing at 134°C – Solid symbols: parallel direction – Outline symbols: perpendicular direction.

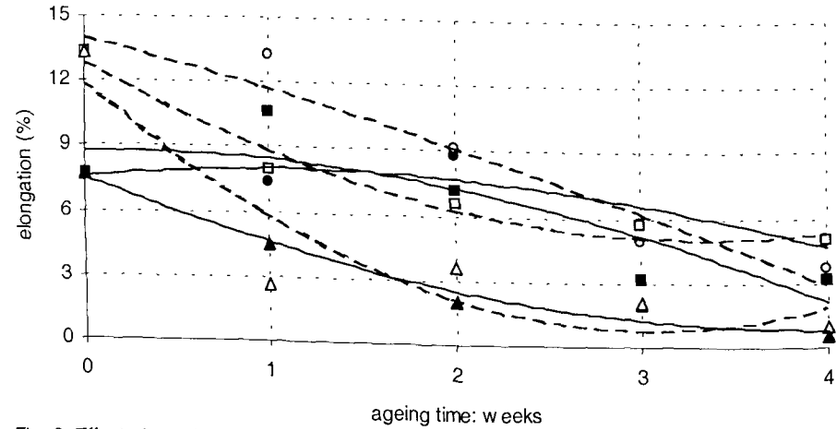

Fig. 6: Effect of accelerated heat ageing at different temperatures on the elongation at break of modern parchment.

Table 1: Some mechanical properties of historical parchment.

	Tensile strength (N/mm2)	Elongastion at break (%)
Tanta Excavation sample 1	2.35	4.0
Tanta Excavation sample 2	1.99	2.2
Tanta Excavation sample 3	2.141	3,1

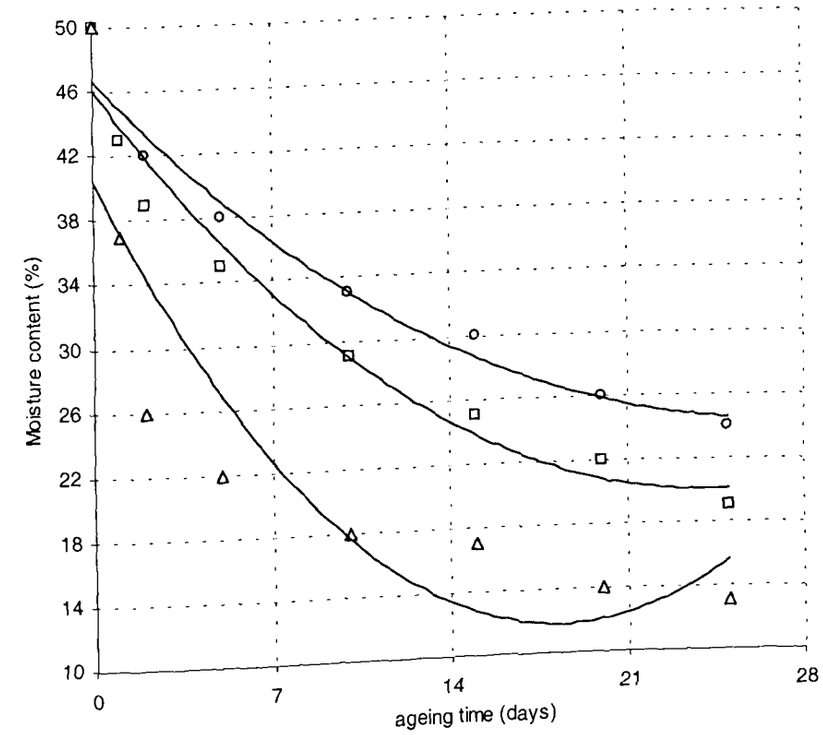

Fig. 7: Determination of humidity sorption at 95 % RH, 20°C of modern parchment before and after accelerated ageing at: ○ 70°C – □ 100°C – Δ 134°C.

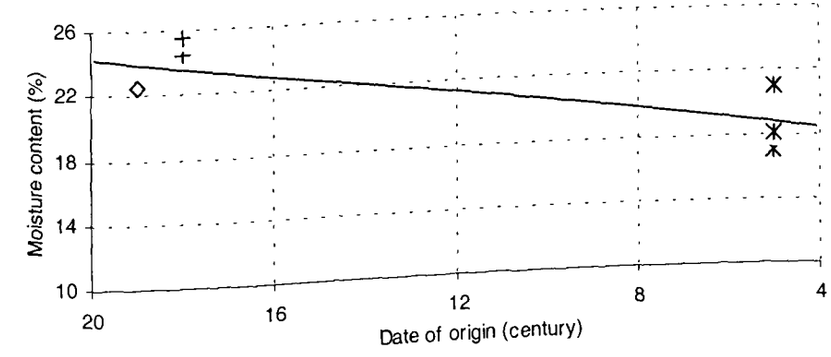

Fig. 8: Determination of humidity sorption at 95 % RH, 20°C of historical parchment. ◊ Samples of the Medical Library – + Samples of Tanta Excavation – ✱Samples of the Coptic Museum.

increasing deterioration. In our case the loss percentage after 25 days was 52% at 70°C, 62 % at 100°C and 74 % at 134°C. Fig. 8 shows that the humidity sorption of historical samples is distinctly lower, i.e. on a level that is reached for modern parchment after longer accelerated ageing at high temperature only. It was noted that relatively high sorption of moisture was obtained from parchment manuscripts from Tanta Excavation and low sorption of moisture was obtained from parchment manuscripts from Coptic Museum. Hallebeek[20] proved that for artificially aged samples there is a general tendency for the amount of total moisture to fall when the samples are more degraded, but that for natural (historical) samples the percentage of total moisture content is higher when the degree of degradation is higher. An explanation for the deterioration mechanism of water absorption of artificial aged and historical parchment could be as follows: water is present in parchment in three forms, free, associated and bound. The occurrence of bound water acts as protection against denaturation, whereas associated and free water are reserve sources[20, 21]. Bound water is held by strong chemical bond in polar groups in the protein molecules, while free water is held by capillary forces. The amount of free water, depend on the formative structure of the parchment fibres and the porosity of membrane. The force, which coheres bound water with protein molecule is much greater than the force which coheres free water with walls of capillary pores in parchment. This indicates that the ability of parchment to lose free water is much greater than its ability to lose bound water. Therefore, it can be said that the amount of free water depends on humidity, and the variation in free water content depends on environmental conditions. The amount of bound water depends on the chemical and physical properties of the protein molecule. The parchment continues to retain bound water if it is not exposed to dryness or high temperature. The loss of free water in parchment results in a loss of softness, while the loss of bound water results in its deterioration, due to changes that occur in its chemical structure and physical properties. In our study we found that the ability of new parchment to absorb humidity was about 50% higher than that of historical parchment, while the decrease during accelerated ageing was 52%, 62 % and 74 %, depending on the ageing temperature (cf. Fig. 7).

Change of Colour

Colour by definition has three dimensions. The first is known as reflectance, also defined as value of lightness. The second dimension of colour is known as hue. Hue is the attribute of colour that distinguishes green from red and blue from yellow. The third dimension of colour is saturation of chrome.

Table 2: Change of colour parameters of modern parchment after accelerated ageing at different temperatures.

	Ageing at	Weeks 0	1	2	3	4
ΔL	70°C	84,23	0,67	1	4,01	5,06
	100°C	85,66	3,22	3,93	5,81	14,57
	134°C	82,20	7,56	11,58	15,88	17,19
Δa	70°C	22,78	-3,03	-6,11	-15,46	-27,42
	100°C	19,91	-10,73	-12,57	-18,39	-40,12
	134°C	30,19	-12,02	-33,43	-52,63	-57,05
Δb	70°C	17,60	-2,52	-5,43	-12,95	-22,71
	100°C	16,19	-8,51	-9,32	-15,62	-13,76
	134°C	17,92	-14,08	-22,49	-25,1	-29,48
ΔE	70°C	89,01	4,00	8,24	20,56	35,96
	100°C	89,42	14,07	16,13	24,82	44,85
	134°C	89,39	19,99	41,91	60,43	66,47

The colour we see ranges from violet (400 to 430 nm), blue (430 to 458 nm), green (485 to 570 nm), yellow (570 to 585 nm), orange (585 to 610 nm), to red (above 610 nm). This range comprises what is known as the visible spectrum. Qualitatively, the nature of a colour change can be understood by examining the visible reflectance spectrum before and after the sample has been exposed to artificial heat ageing. The colour change is indicated by the change in the spectrum[22].

From colour measurement data (Fig. 9) it becomes clear that the values of the brightness (value L) decreased with an increase in temperature during ageing. The reduction of the brightness after four weeks of ageing in relation to the brightness before ageing was 6 % at 70°C, 17 % at 100°C and 21 % at 134°C (cf. Table 2). At 70°C and 100°C the decrease was slow during the first two or three weeks, while at 134°C the reduction increased continuously during the whole period of ageing. All historical samples are significantly darker than the modern ones even after the longest period of ageing at the highest temperature.

The a-value increased with increasing temperature during the course of ageing, indicating that the colour of the samples is changing towards red during ageing. Regarding the historical samples, the a-values of the Tanta excavation samples are as high and even higher than the a-values of modern parchment after a

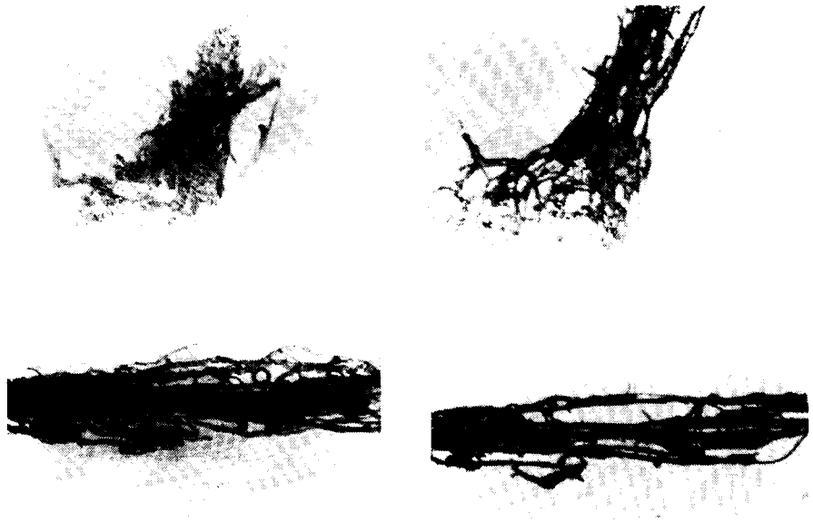

Fig. 4: Microscopical pictures of historical parchment at room temperature (left column) and at shrinkage temperature (right column). 1,2: the Tanta excavation sample; 3,4: the Coptic Museum sample.

Shrinkage

The results proved that heat ageing affected the collagen of the parchment, which is clearly reflected in the shrinkage temperature, considering that parchment of the control sample (before ageing) presents a shrinkage temperature of 54°C. The reduction in shrinkage temperature of aged modern parchment (Fig. 1 and 3) after 4 weeks at 70°C was 13 %, at 100°C 17 % and at 134°C 28 %. From the data (Fig. 2 and 4) it becomes clear that the reduction in the shrinkage temperature of historical parchments compared with the control sample differs from place to place. The final results also show that all the historical parchments have suffered from degradation, more so than those which were artificially aged. The reduction of the shrinkage temperature of the historical parchments by comparison with modern parchment (before ageing) was as follows:

- Certificate from the Faculty of Medicine Library (Cairo University), sample 1 and 3: 29 %.
- Certificate from the Faculty of Medicine Library (Cairo University), sample 2: 28 %.
- Manuscripts from Tanta excavation, sample 1: 35 %.

- Manuscripts from Tanta excavation, sample 2: 33 %.
- Manuscripts from Tanta excavation, sample 3: 33 %.
- Manuscripts from Coptic Museum, sample 1: 38 %.
- Manuscripts from Coptic Museum, sample 2: 36 %.
- Manuscripts from Coptic Museum, sample 3: 35 %.

MECHANICAL PROPERTIES

It becomes clear from Fig. 5 and 6 that there is a significant reduction in mechanical properties (tensile strength and elongation) for both aged and historical samples in perpendicular and parallel directions as compared with samples before ageing. The percentage loss of tensile strength after four weeks is:

- at 70°C in perpendicular direction: 29 %; in parallel direction 60 %;
- at 100°C in perpendicular direction: 51 %; in parallel direction 70 %;
- at 134°C in perpendicular direction: 88 %; in parallel direction 87 %.

The percentage loss of elongation after four weeks is:

- at 70°C in perpendicular direction: 72 %; in parallel direction 37 %;
- at 100°C in perpendicular direction: 62 %; in parallel direction 59 %;
- at 134°C in perpendicular direction: 92 %, in parallel direction 93 %.

The effect of heat on tensile strength at 70°C and 100°C after one week is quite different in the perpendicular and in the parallel directions, but, as can be seen from Fig. 5, after two and after four weeks these differences almost disappear. At 134°C there are already no differences after one week.

The historical samples (Table 1) show significantly lower tensile strength and elongation. The reduction in mechanical properties is due to the decrease in distance between the polypeptide chains, resulting in the strengthening of cross-links and the eventual deformation of the gross structure. The increased proximity of the chains is initiated by the loss of water. Water molecules no longer form bridges between adjacent chains, or natural plasticizers, such as small amounts of grease and fatty substances, may be removed or decay.

HUMIDITY SORPTION

From Fig. 7 it can bee seen that humidity sorption of new parchment at 95 % RH, and 20°C is quite high, and that it decreases with an increase in temperature during ageing. Larsen[19] proved that the total humidity sorption curve decreases with

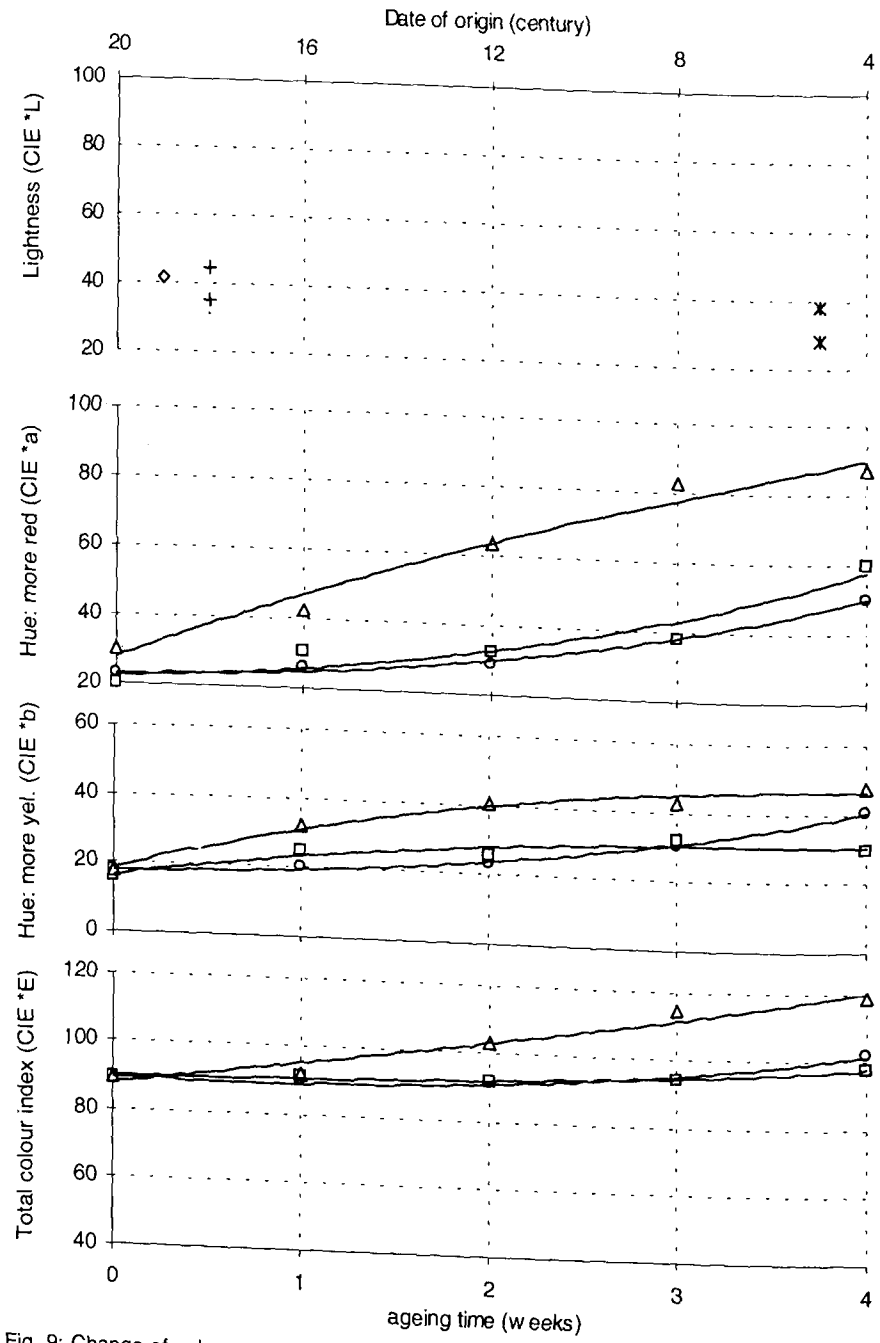

Fig. 9: Change of colour parameters of modern parchment during accelerated ageing at different temperatures: ○ 70°C – □ 100°C – △ 134°C.

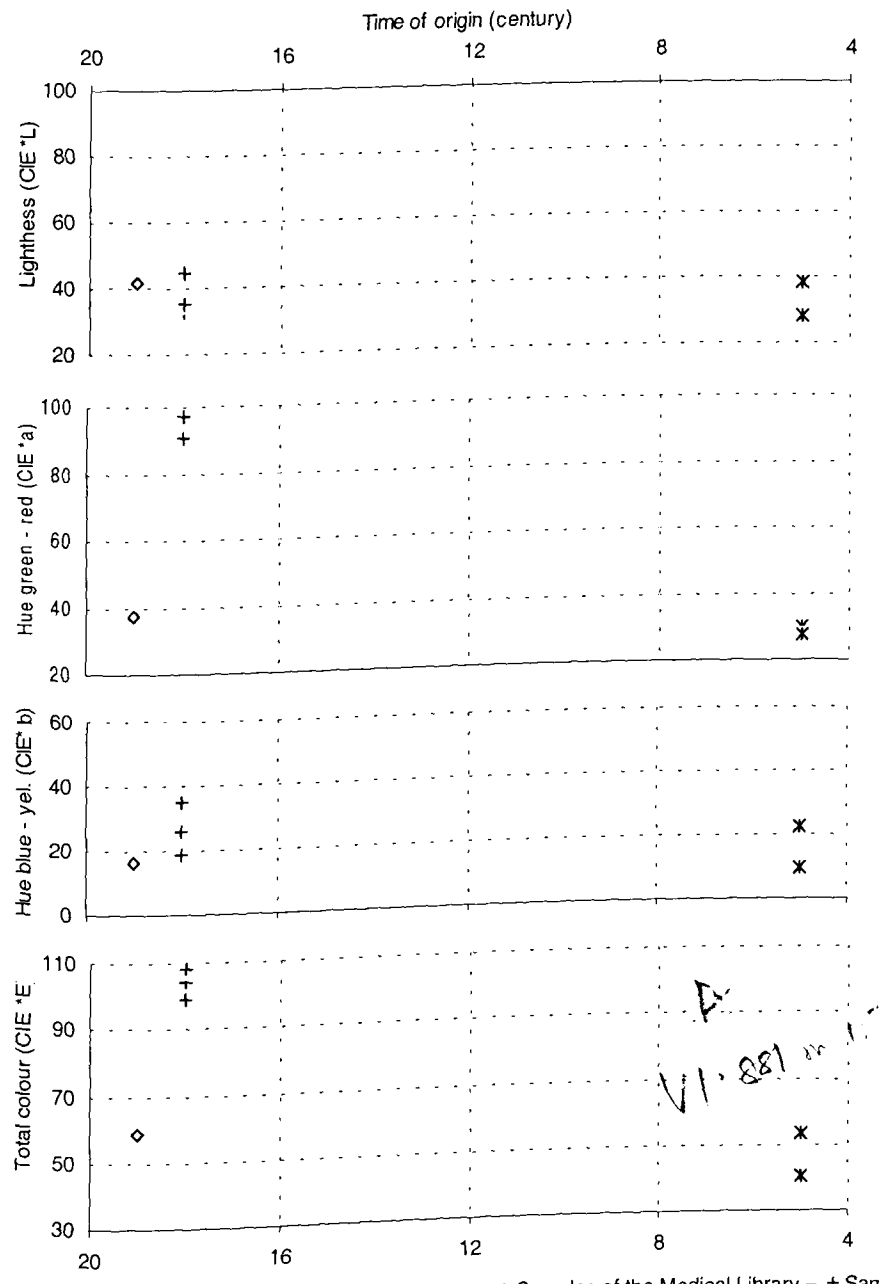

Fig. 10: Colour parameters of historical parchments. ◊ Samples of the Medical Library – + Samples of Tanta Excavation – ✱ Samples of the Coptic Museum.

longer period of ageing at the highest temperature. During the two or three centuries of their history these parchment samples must have suffered very aggressive conditions, comparable to the harshness of longer accelerated ageing at high temperatures.

The yellow colour (value b) also increased with increasing temperature during ageing, but not as much as the a-value. Accelerated ageing seems to provoke reddening of parchment more than a yellowing. Most striking is the fact that the b-value of the historical parchment samples has not increased with their age. One of the oldest samples (Coptic Museum no.1) is significantly less yellow than any of the modern samples even before ageing.

Discussion

Measurement of shrinkage temperature of heat aged and historical parchment shows that there is a clear connection between the shrinkage temperature and the chemical changes in the studied samples due to deterioration. In the historical samples, used for this study, shrinkage takes place at a much lower temperature, in one of the Coptic Museum samples close to 33°C.

From the physical point of view, the most important characteristics of collagen are the way in which fibres swell in solutions and the way in which they shrink at a definite temperature. When collagen is denatured, i.e. when its helical structures, though not necessarily its components, are destroyed, it forms gelatin; a familiar substance, but unusual among proteins in so far as it has no internal ordered structure.

An explanation for the shrinkage temperature process, according to Southward[23], is as follows; collagen stability is largely dependent on the highly ordered, semi-crystalline structure of the fibril, which is stabilized predominantly by intramolecular hydrogen bonds between peptides of the triple helical collagen molecule. Loss of stability can occur in the following manner.

When a collagen sample is in an aqueous medium, water easily penetrates the collagen molecule due to its affinity for the hydrogen bonding sites in the amorphous areas. The presence of water increases the spacing between the collagen chains. Macroscopically, this effect is seen as a swelling of the sample in question. If the sample is then heated at a certain temperature, the thermal energy will become sufficient to break the hydrogen bonds in the amorphous areas holding the polypeptide chains together, each individual chain then folds into random coils, and the hydrogen macromolecule loses its ordered structure and denatures. Collagen which has denatured has lost its partially crystalline nature, as can be evidenced under polarized light by a loss of birefringence.

On the basis of the study, it can be noted that the physical disintegration of both artificially and naturally aged parchment is caused by competition and interaction of the oxidative breakdown of collagen in limed parchment. The cause of the oxidative breakdown is mainly due to environmental factors, such as heat for artificially aged parchment, and several combined factors (heat, light etc) for historical parchment.

The shrinkage tempera ture of historical parchment samples is distinctly lower than that of the modern parchment samples, even after sharp accelerated ageing (134°C) over a longer period (4 weeks). We observed only little difference between die shrinkage temperature of the samples from the Tanta Excavation and the samples from the Coptic Museum, despite there being more than a 1000 years age difference between them. The main reason for this are the aggressive conditions of the excavation site compared to the environmental conditions in the museum collection. The effectiveness of the first conservation treatment, i.e. a temporary treatment in the excavation area, may also contribute. The lack of a report on the historical circumstances of the Tanta Excavation makes it impossible to take account of the conditions in which the parchment had lain buried and/or the conditions before and after arrival in the museum collection.

Some parts of the parchment are apparently less hydrothermally stable than others because of pertubation or deterioration of their crystalline and ordered amorphous structure. The less stable regions begin to shrink at lower temperatures, whereas the more stable regions denature at higher temperatures approaching more normal shrinkage temperature (T_s) values. A similar description applies for fibers. The total fibril deterioration in each fiber varies, and, therefore some fibers begin to shrink at a lower temperature than others. Larsen[19] has shown that the cause for loss in hydrothermal stability of the old historical samples can be ascribed to several combinations of the two main breakdown mechanisms. In general this is:

- Strong oxidation and strong acid hydrolysis,
- Strong oxidative and less hydrolysis,
- Strong acid hydrolysis and less oxidation.

Larsen[19] reports that the differences in the hydrothermal stability of fibres in a sample may be ascribed to three main factors:

- Differences in stability due to initial treatment of the skin;
- Non-uniformity in production;
- A non-uniform degree of deterioration.

It has been shown that the importance of the three reasons for differences may be arranged in the order $3 > 2 > 1$.

These results have been confirmed by many authors. Chahine and Rottier[24] reported that when the structure of collagen is damaged by oxidative breakdown, there appear to be fewer and weaker hydrogen bonds maintaining the structure. Under these circumstances less thermal energy is needed to break the remaining hydrogen bonds and, therefore, fibre shrinkage occurs at a lower temperature. Larsen[25] proved that shrinkage temperature decreases during ageing.

Conclusions

- When modern parchment is heated, the fibres of collagen tolerate temperatures at 70° C and 100° C for four weeks, but at 134° C the parchment breaks down into very small lengths which, under the further action of the same heat for a long time (more than four weeks), change into a complex material by the process of oxidation.
- Several properties of artificially heat aged modern parchment samples increase during ageing and as the temperature increases. For historical samples, these changes depend on many factors, and depend more on the condition of the surrounding environment than on the age of a sample.
- A study of moisture sorption characteristic of parchment is a useful indication of its relative state of degradation. The relationship between equilibrium moisture content and relative humidity would reveal more information than just the total water content. Modern parchment absorbs moisture more than both artificially heat aged and historical. The ability of modern parchment to absorb humidity is decreased with longer time and higher temperature of accelerated ageing. The ability of very old historical parchment to absorb humidity is better than that of modern parchment after heat ageing at high temperature (134° C) for less than two weeks. This is due to the structure and properties of historical samples.
- Another possible method of estimating the degree of degradation would be to measure shrinkage temperature. The hydrothermal stability of parchment is decreased as the time of ageing and temperature are increased. For historical samples the reduction depends on the condition of the object in archaeological sites.
- For microscopically observing shrinkage temperature, only minute samples of collagen fibres are required, which is a great advantage for research in historical parchments. Samples of only 0.1 to 0.5 mg are needed. Therefore, the measurement of hydrothermal stability using a polarizing microscope with the hot table technique can be considered as being practically a non-destructive method.
- Measurements of the shrinkage temperature of historical samples proved that the percentage loss of hydrothermal stability was high. This is a clear indication that all historical samples studied are in a bad condition, depending from their age: the lowest shrinkage temperature was found with the samples from the Coptic Museum (5th century), followed by the samples from the Tanta Excavation (18th century), while the shrinkage temperature of the samples from the Library of Faculty of Medicine (19/20th century) was nearer to that of samples after prolonged accelerated ageing at very high temperature.
- It is clear from this study that most archaeological sites in Egypt need to draw up a plan for monitoring the condition of parchment manuscripts.

Acknowledgement

We would like to thank Mr. Waldemar Zuk for his help and suggestions.

Summaries

Changes in Some Properties of Aged and Historical Parchment

The starting point for the research reported here is the poor state of parchment documents at many sites in Egypt: museums, stores, libraries and excavation areas. Modern parchment samples were submitted to accelerated ageing at different temperatures (70°, 100°, 134° C). Several properties (shrinkage temperature, mechanical strength, humidity sorption, colour change) were measured and compared with the same properties of historical parchment samples from the 5th, the 18/19th and the 20th centuries. The applied methods seem to be apt to determine the state of deterioration, which is considered the first step of conservation.

The shrinkage temperature was measured using the micro-hot table technique, which is considered to be a non-destructive method because only very small samples are needed for the measurements.

Modifications de certaines propriétés du parchemin ancien et historique

Le point de départ de l'étude exposée ici se situe dans le triste état des objets en parchemin tels qu'ils sont conservés dans beaucoup d'endroits en Egypte : dans les musées, les bibliothèques, sur les sites de fouilles archéologiques et chez les antiquaires. Des échantillons de parchemin moderne ont été soumis au vieillissement accéléré à différentes températures (70°, 100°, 134° C).

Certaines propriétés (température de contraction, résistance mécanique, absorption de l'eau, modification de la couleur) ont été mesurées et comparées avec les propriétés correspondantes du parchemin historique du 5ème, 18/19ème et du 20ème Siècle. Les méthodes appliquées semblent

être adaptées pour évaluer l'état de détérioration du parchemin, ce qui constitue le premier pas vers la restauration. La température de contraction a été mesurée selon la technique de la microplatine chauffante. Cette méthode peut être considérée comme non-destructive car elle ne requiert que de très petits échantillons pour effectuer les mesures.

Änderungen in einigen Eigenschaften von gealtertem und historischem Pergament

Der Ausgangspunkt für die Untersuchung, über die berichtet wird, ist der schlechte Zustand der Objekte aus Pergament in vielen Aufbewahrungsorten in Ägypten, in Museen, Bibliotheken, an Ausgrabungsstätten und bei Antiquitätenhändlern. Proben modernen Pergaments wurden einer beschleunigten Alterung bei verschiedenen Temperaturen (70°, 100°, 134° C) unterworfen. Bestimmte Eigenschaften (Schrumpfungstemperatur, mechanische Festigkeit, Wasseraufnahme, Farbänderung) wurden gemessen und mit den entsprechenden Eigenschaften von historischem Pergament aus dem 5., 18./19. und dem 20. Jahrhundert verglichen. Die gewählten Untersuchungen scheinen geeignet zu sein zur Bestimmung des Abbauzustands von Pergament, was als erster Schritt zur Konservierung gilt.

Die Schrumpfungstemperatur wurde auf einem Miniatur-Heiztisch gemessen. Diese Methode kann als nicht maaterialzerstörend gelten, weil nur sehr kleine Proben dafür benötigt werden.

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Permanence of Paper 2:
Correlation between Permanence of Paper Made from Straw Pulps and Ageing Variables

by HOUSSNI EL-SAIED, ALTAF H. BASTA & MONA M. ABDOU

Introduction

Today two generally different methods are used to ensure the preservation of the written or printed word: preservation of the object itself and format conversion, that is microfilming, electrostatic copying or other methods of reproduction. Direct preservation is the most common method, preserving the paper after the information has been printed on it. This includes lamination, paper splitting and related methods if the paper has already significantly lost its mechanical strength, specific chemical treatments for slightly damaged and endangered paper, cold storage, and the use of permanent paper[1].

Permanent paper is paper that can have a reasonable life expectancy of 200 years or more[1]. Rasch[2] proposed that the percentage of folding endurance after 3 days at 100°C should be termed the "permanency factor".

The use of permanent paper for books and documents of lasting importance and value is, obviously, the most practical method that can be used to ensure the preservation of the printed word. The grades of paper that have the greatest permanence are those made from pulps that have high copper ammonium viscosity, high alpha-cellulose content, low copper number, low lignin content, low pentosan and low gamma cellulose content. The average degree of polymerization (DP) of cellulose is the most important factor that affects permanence and should be at least 1000 to 1200[3]. The copper number must not exceed 1.0, since colour reversion appears to increase with copper number, as well as with β- and γ- cellulose content[4]. In the relevant technical literature it is said that the type of bleaching is important, too, i.e. that chlorine dioxide bleached pulps are more permanent than those bleached with hypochlorite; and slightly bleached sulfite pulps are more colour stable than highly bleached sulfite pulps[5]. Sulfite pulps are generally considered to be more stable than sulfate pulps[5], even if the ageing quality of some sulfate pulps has been reported to be comparable to that of rag.

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Rag papers are generally estimated to have the highest permanence of all kinds of paper used as information carrier. Wood pulp can made as colour stable as rag stock[6] under special conditions. Mixed rag and refined chemical wood fibers with alkaline filler are specified for many grades of permanent papers[7]. It is believed, however, that for the greatest longevity, permanent paper must be made from cotton or linen rag fibers.

In countries, such as Egypt, deprived of extensive forests, the agricultural residues, such as straws and sugarcane bagasse etc, are often used as alternative sources of fibrous raw materials for the production of paper pulps. The soda and kraft pulping processes are the methods most used for the production of these pulps. In most paper mills long fiber wood pulp is added to rice straw and/or bagasse pulps to improve the quality of the paper produced. Unfortunately, at present the sizing process for writing and printing papers is carried out at low pH (~ 3.65) by using rosin as a sizing agent together with alum. This acidity, together with the relatively low α-cellulose and low DP of pulps from the given agricultural wastes, are recognized contributory factors to a decrease in paper permanence[3, 8].

In our previous work[9] it became clear that neutral sized wood pulp paper sheets, compared with acidic sized wood pulp paper sheets, have a higher optical and mechanical permanence either by adding sodium silicate to the sizing system or by minimizing the amount of added alum This article studies the possibility of making permanent papers from local Egyptian raw materials. It looks at relevant criteria for the manufacture of such papers from local agricultural wastes and papers made from imported wood pulp and compares the effect of pH from different sizing systems on the optical and mechanical properties of these papers after artificial ageing. The change in the chemical, optical and mechanical properties with sizing systems of differing pH levels and ageing time was clarified and correlated by polynomial models.

Experimental

Paper sheets used

- RSP: Paper prepared from rice straw soda pulp produced at RAKTA Paper Mill, Alexandria.
- BP: Paper prepared from bagasse kraft pulp, produced at Edfo Pulp Mill, Upper-Egypt.
- WP: Paper prepared from bleached imported kraft softwood pulp.

- MP: Paper prepared by blending 60% rice straw soda pulp, 20% bagasse kraft pulp and 20% imported kraft softwood pulp.

The pulps (bagasse and rice straw) were first bleached according to the three-stages system CEH (chlorination, alkali extraction, hypochlorite). The bleached local pulps and softwood pulp were chemically and physically analyzed for α-cellulose[10], pentosans[11], lignin[12], ash content and degree of polymerization (DP)[13] (Table 1). The paper sheets were prepared according to the method described in part 1 of our research[9] and the sizing system is shown in Table 2. Table 3 gives the chemical, physical and optical qualities of paper sheets made from the pulps without sizing.

Table 1: Properties of the pulps

	Rice straw (RSP)	Bagasse (BP)	Wood pulp (WP)
α-cellulose (%)	71.22	77.6	87.62
Pentosans (%)	17.40	20.70	6.90
Lignin (%)	1.32	0.67	Traces
Ash content (%)	3.31	0.43	0.16
Degree of polymerization	686	772	843

Table 2 : Sizing system of the papers (% based on weight of pulp)

	Rosin	Alum		Rosin	Alum	Sodium Silicate
pH 3.65	0.0	5.6	pH 6.75	2.74	1.84	
pH 4.8	2.74	5.6	pH 7.0	2.74	1.84	0.6

Table 3: Properties of unaged paper sheets made from the pulps without sizi ng

	Rice straw (RSP)	Bagasse (BP)	Wood pulp (WP)	Mixed pulp (MP)
α-cellulose (%)	65.91	64.71	74.50	70.13
Carbonyl content (mM/100g)	5.60	16.00	13.60	6.00
Degree of polymerization	935.16	982.72	862.67	880.93
Brightness (%)	77.50	78.80	89.00	78.00
Whiteness (%)	77.40	79.10	88.40	78.50
Opacity (%)	69.35	67.80	67.50	68.43
Number of double folds	50	100	250	80
Tear factor	53.10	52.90	128.30	71.20
Burst factor	60.20	58.10	84.50	82.10
Breaking length (m)	4200	4959	4467	4005

Ageing and properties of the sample paper sheets

Unsized and sized paper sheets from the different pulps were artificially aged using dry thermal accelerated ageing in an oven at 100° C, for several cycles: 3, 6 and 12 days. The unaged and the aged paper sheets were chemically and physically analyzed for α-cellulose[10], carbonyl content[14, 15], degree of polymerization[13] and sizing[16]. They were also tested for optical properties (whiteness, brightness, opacity) and mechanical strength[17] (double folds, tear and burst factors, breaking length).

Experimental design

The two following variables were chosen:

- pH of sizing system during paper sheet formation: pH 3.65–7.0
- Time of artificial ageing: 0–12 days.

The design used was a two factor rotatable design, with $\alpha = 1.414$[18].

In order to correlate the ageing variables, such as pH-value (X_1) and time of ageing (X_2), with the values of chemical, optical and strength properties of paper sheets (Y) the following polynomial model was proposed:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_{11}X_1^2 + b_{22}X_2^2 + b_{12}X_1X_2$$

The regression constant b_0 and the coefficients $b_1 \rightarrow b_{12}$ of the above model were obtained using multiple regression analyses[18].

RESULTS AND DISCUSSION

Figs. 1–11 show the same properties as given in Table 3 independent from the two ageing variables, while percentages of the change in properties are given in Table 4. Table 5 shows the values X_1 and X_2 which give the optimum responses.

Effect of ageing variables on chemical properties

Fig. 1 shows the change of α-cellulose caused by thermal ageing. At a constant pH (left column) the α-cellulose content decreased when the ageing time was increased. This is attributed to the inclination of cellulose long chains to decompose via cleavage at the glycosidic linkage between the C_1 and oxygen molecule[19]. It can be seen that for all the four pulps the α-cellulose content gen-

Table 4a: Percentages of change in chemical, optical and physical properties of paper sheets made from different pulps with different sizing systems before and after accelerated ageing in relation to unsized and unaged sheets.

		Rice straw				Bagasse			
	pH days:	0	3	6	12	0	3	6	12
α-cellulose	3.65	-2.25	-3.58	-3.88	-5.42	0.4	-2.7	-4.51	-5.83
	4.8	-1.4	-3.3	-4.3	-8.06	-0.73	-2.69	-2.952	-8.314
	6.75	-1.17	-1.47	-1.79	-3.03	1.02	0.56	-0.062	-3.35
	7	-1.05	-1.23	-3.46	-4.79	1.39	0.32	-2.3	-5.61
Carbonyl content	3.65	14.3	300	728.6	-28.6	-50	30	130	-90
	4.8	28.6	500	557.1	-28.6	115	120	260	-90
	6.75	357.1	471.43	328.6	14.3	-60	90	70	-75
	7	42.9	371.41	342.9	-71.4	-30	75	60	-80
DP	3.65	13.2	1.15	-14.5	-31.4	-3.012	-10.4	-28.3	-28.4
	4.8	-3.9	-12.7	-34.9	-38.2	-13.5	-17.2	-41.06	-42.04
	6.75	2.3	-8.2	-26.6	-36.8	-11.66	-17.04	-29.5	-31.21
	7	3.8	-19.95	-24.9	-27.72	2.93	-14.53	-25.92	-30.7
Brightness	3.65	-4	-10.5	-17.74	-19.36	-2.92	-5.46	-6.6	-15.23
	4.8	-6.6	-12.8	-16.5	-17.03	-4.7	-6.98	-7.5	-9.65
	6.75	-6.97	-12	-14.32	-15.9	-7.23	-5.96	-10.4	-10.4
	7	-5.81	-10.2	-12.4	-14.71	-6.6	-10.8	-11.3	-11.7
Whiteness	3.65	-3.5	-11.2	-19.3	-19.8	-2.91	-4.8	-6.5	-15.3
	4.8	-5.94	-12.4	-15.65	-16.2	-4.2	-7.2	-7.3	-9.61
	6.75	-6.5	-12.02	-12.53	-15.4	-8.3	-5.6	-9.7	-10.5
	7	-5.3	-11.2	-12.2	-14.5	-6.8	-8.7	-10.6	-11.1
Opacity	3.65	-3.1	-8.44	-8.3	-12.5	0.6	-2.4	-4.9	-6.1
	4.8	0.2	-9.2	-11.6	-16.7	3.54	-2.21	-4.7	-7.5
	6.75	-0.8	-7.14	-9.88	-17.1	0.4	-0.3	-4.9	-9.3
	7	-2.7	-9.9	-13.2	-17.5	-1	-2.4	-7.5	-10.5
Fold number	3.65	-40	-40	-40	-60	-50	-70	-70	-80
	4.8	60	0	-20	-40	-60	-60	-60	-70
	6.75	60	60	40	20	-50	-50	-50	-60
	7	20	20	20	0	0	-40	-40	-60
Tear factor	3.65	35.8	2.26	2.26	-22.6	27.8	-10.96	-21.9	-32.9
	4.8	149.5	64.97	30.1	7.2	122.5	44.99	11.7	-7.9
	6.75	72.5	60.8	49.7	12.4	37.1	14.8	3.4	0.95
	7	72.9	36.9	36.91	25.6	38.2	3.8	-1.7	-7.2
Burst factor	3.65	-36.6	-17.4	-20.4	-23.09	-37.9	-37.7	-37.5	-25.3
	4.8	-14.6	-29.9	-13.23	3.32	-19.8	-16.7	-19.6	-10.2
	6.75	-4.3	2.33	0.32	3.32	12.7	-7.9	13.4	10.5
	7	1.8	15.1	3.16	0.7	4.5	1.6	20.3	2.1
Breaking length	3.65	-11.3	-18.1	-17.7	-17.3	-28.92	-28.8	-34.54	-34.3
	4.8	-3.5	-3.1	-3.1	-21	-16.88	-22.7	-10.65	-16.2
	6.75	16.8	9.4	6.4	2.6	-8.6	-8.3	4.2	4.8
	7	1.5	9.5	2.4	3.2	16.8	10.8	11.13	11.313

Table 4b: Continuation

		Wood pulp				Mixed pulp			
	pH	0	3	6	12	0	3	6	12
α-cellulose	3.65	-0.4	-2.1	-2.2	-2.32	-1.29	-4.4	-5.86	-3.15
	4.8	-0.74	-5.7	-5.87	-9.5	0.696	-4.94	-7.43	-11.62
	6.75	-0.85	-1.8	-2.35	-4.66	-0.73	-3.15	-4.38	-9.13
	7	-1.75	-1.8	-2.15	-4.31	-1.84	-3.8	-6.26	-6.96
Carbonyl content	3.65	-23.5	88.2	170.6	-88.2	273	273.3	513	33.3
	4.8	-52.9	158.8	76.5	-88.2	60	460	513	207
	6.75	-64.7	88.2	88.2	-52.9	33	433	300	-73
	7	-17.6	100	117.6	-58.8	-20	340	313	-6.7
DP	3.65	-17.34	-9.9	-24.4	-36.51	0.003	-5.2	-23.8	-30.7
	4.8	-12.94	-16.88	-32.4	-32.72	0.003	-4.15	-26.5	-35.42
	6.75	-9.9	-25.5	-30.86	-33.97	3.3	-9.899	-39.3	-40.3
	7	-21.57	-26.53	-29.93	-30.3	3.3	-4.32	-25.65	-28.05
Brightness	3.65	-4.94	-7.8	-12.5	-18.43	-1.03	-8.9	-16.9	-17.7
	4.8	-6.74	-10.6	-14.3	-15.2	-8.21	-11.5	-15.6	-16.54
	6.75	-4.94	-5.17	-12.58	-14.16	-5.9	-12	-12.7	-13.7
	7	-5.6	-9.1	-11.24	-12.81	-4.9	-10.8	-12.31	-12.44
Whiteness	3.65	-3.96	-7.01	-10.63	-17.42	-1.15	-8.8	-17.4	-18.09
	4.8	-5.54	-9.73	-13.12	-13.91	-7.78	-11.9	-16.82	-17.1
	6.75	-4.41	-4.3	-11.31	-13.23	-6.5	-12.99	-12.99	-14.65
	7	-2.71	-4.75	-9.16	-10.07	-4.84	-11.46	-12.74	-13.76
Opacity	3.65	-0.3	1.6	-0.7	-5.5	1.17	-5.85	-5.7	-10.1
	4.8	8	1.63	-2.7	-4.3	2.34	-7	-9.4	-17.3
	6.75	4.44	2.21	-2.5	-6.81	-1.315	-4.97	-8.8	-13.6
	7	2.7	1.33	-2.22	-5.5	-0.6	-5.8	-9.4	-13.7
Fold number	3.65	4	-8	-36	-56	12.5	0	0	-12.5
	4.8	156	76	32	8	37.5	50	50	62.5
	6.75	248	244	240	144	12.5	0	0	-12.5
	7	92	88	76	56	600	250	150	87.5
Tear factor	3.65	24.7	16.1	-20.7	-25.4	0	-14.5	-22.9	-31.04
	4.8	15.7	5.4	-17.3	-21.5	135.9	29.2	12.9	5.3
	6.75	27.4	19.7	15.2	-18.3	105.1	6.9	8.15	-19.4
	7	15.5	6	14.8	3.3	40	5.6	7.9	-20.4
Burst factor	3.65	-16.7	-14.1	-20.8	15.9	-44.8	-40.4	-46.8	-30.1
	4.8	-0.4	-16.5	-24.4	-20.2	-14.1	-32.6	-28.3	-29.96
	6.75	23.3	0.12	19.5	26.04	4.4	-32.2	-27.5	-24.9
	7	7.1	0.7	-1.2	-11.8	4.8	-19.41	-19.4	-17.1
Breaking length	3.65	-8.0	-11.4	-14.6	-21.5	3.62	-23.97	-6.82	-0.4
	4.8	11.6	11.8	-7.6	-1.0	7.3	0.5	-0.97	11.5
	6.75	37.3	23.8	17.1	24.2	26.4	18.7	17.6	24.2
	7	31.3	24.6	17.9	25.0	40.4	34.9	33.2	33.3

Table 5: Coefficient of multiple correlation and ageing variables of the optimum response properties

	Coefficient of multiple correlation (R)	pH (X_1)	ageing time (X_2)	Percentage of change with respect to the unsized sample (Table 3)
R	α-cellulose	0.938	7	3	-1.23
i	Carbonyl content	0.973	6.75	12	14.29
c	DP	0.934	6.75	3	-8.20
e	Brightness	0.998	7	3	-10.19
	Whiteness	0.966	7	3	-11.2
s	Opacity	0.979	6.75	3	-7.14
t	Fold number	0.890	6.75	3	60
r	Tear factor	0.999	4.8	3	64.97
a	Burst factor	0.815	7	3	14.9
w	Breaking length	0.932	7	6	2.4
	Sizability know	0.960	4.8	3	155
B	α-cellulose	0.945	6.75	6	-0.062
a	Carbonyl content	0.967	3.65	3	30
g	DP	0.979	3.65	3	-10.40
a	Brightness	0.92	3.65	3	-5.46
s	Whiteness	0.936	3.65	3	-4.8
s	Opacity	0.984	6.75	3	-0.30
e	Fold number	0.958	7	3+6	-40
	Tear factor	0.989	4.8	3	44.99
	Burst factor	0.939	7	6	20.30
	Breaking length	0.885	7	6	11.13
	Sizability	0.929	4.8	12	150
	α-cellulose	0.94	7	3	-1.8
o	Carbonyl content	0.929	6.75	12	-52.9
o	DP	0.986	3.65	3	-9.90
d	Brightness	0.994	6.75	3	-5.17
	Whiteness	1.0	6.75	3	-4.30
p	Opacity	0.930	3.65	6	-0.70
u	Fold number	0.884	6.75	3	244
l	Tear factor	0.969	6.75	3	19.7
p	Burst factor	0.933	6.75	12	26
	Breaking length	0.985	7	12	24.98
	Sizability	0.878	6.75	3	165
	α-cellulose	0.986	6.75	3	-3.33
i	Carbonyl content	0.861	3.65	12	33.3
x	DP	0.794	7	3	-4.32
e	Brightness	0.996	3.65	3	-8.9
d	Whiteness	0.975	3.65	3	-8.8
	Opacity	0.977	6.75	3	-4.97
p	Fold number	0.844	7	3	250
u	Tear factor	0.990	4.8	3	29.20
l	Burst factor	0.927	7	3	-19.5
p	Breaking length	0.916	7	3	34.2
	Sizability	0.988	6.75	6	150

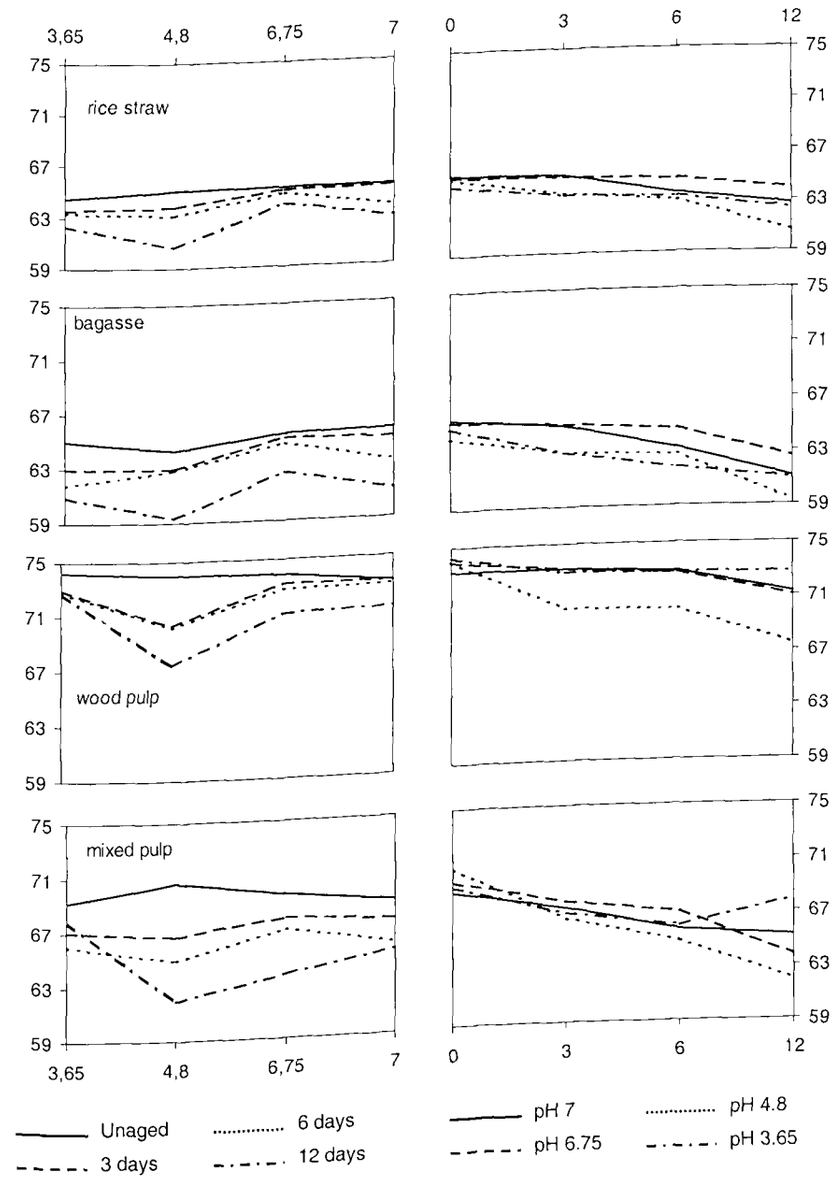

Fig. 1: Relation between the ageing variables (pH: left column; ageing time, i.e. days: right column) and α-cellulose content (ordinate axis).

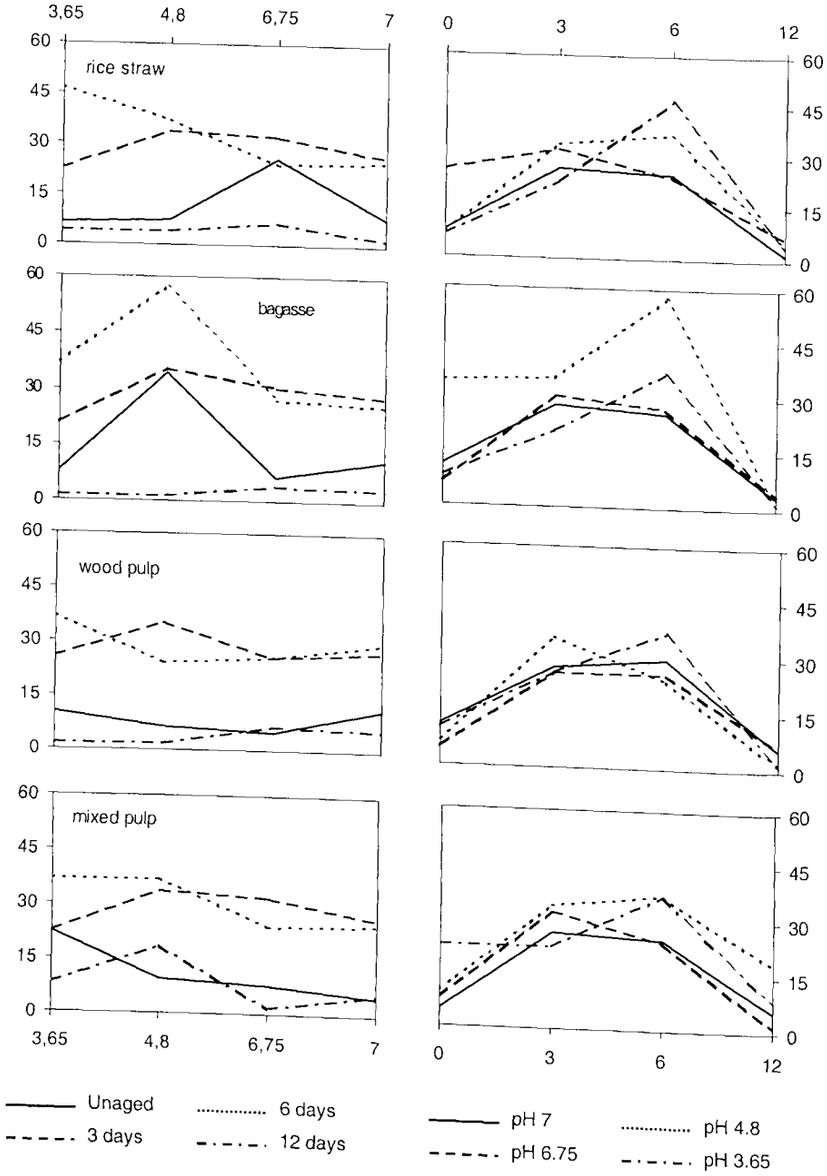

Fig. 2: Relation between the ageing variables (pH: left column; ageing time, i.e. days: right column) and carbonyl content (ordinate axis).

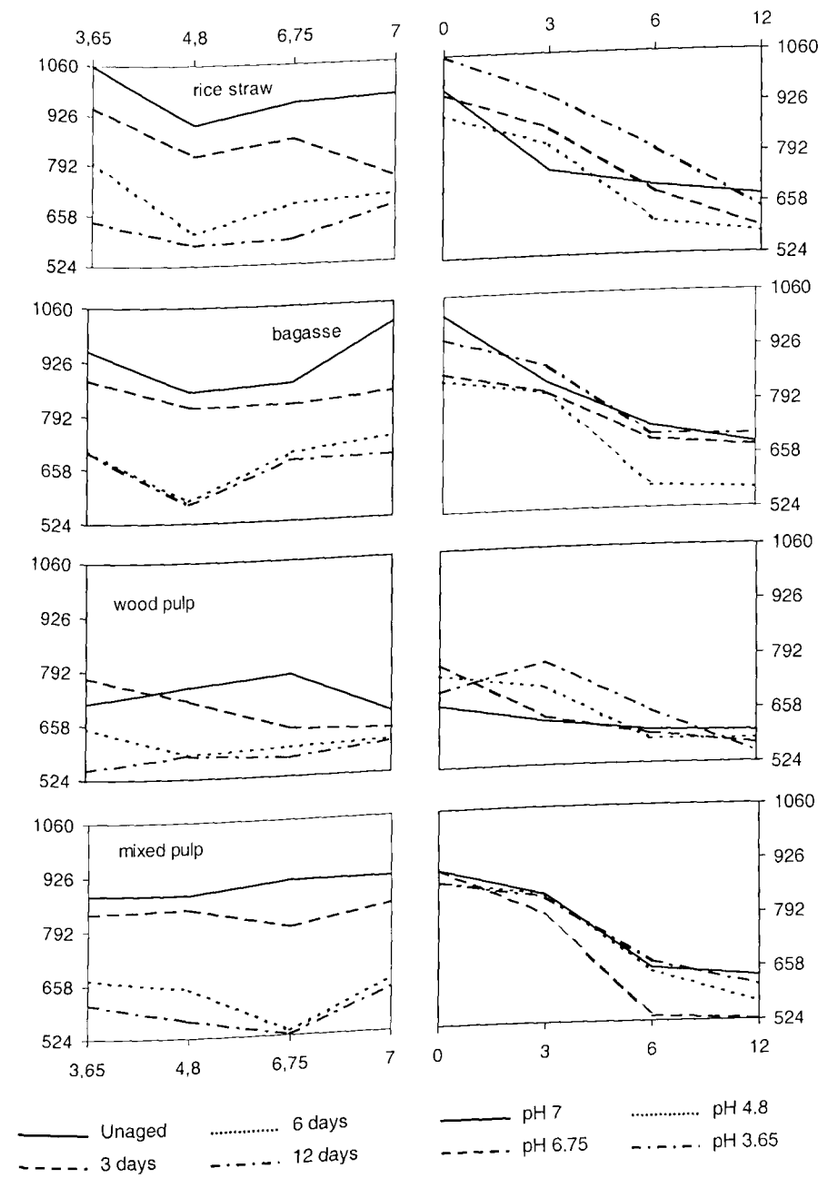

Fig. 3: Relation between the ageing variables (pH: left column; ageing time, i.e. days: right column) and degree of polymerization (ordinate axis).

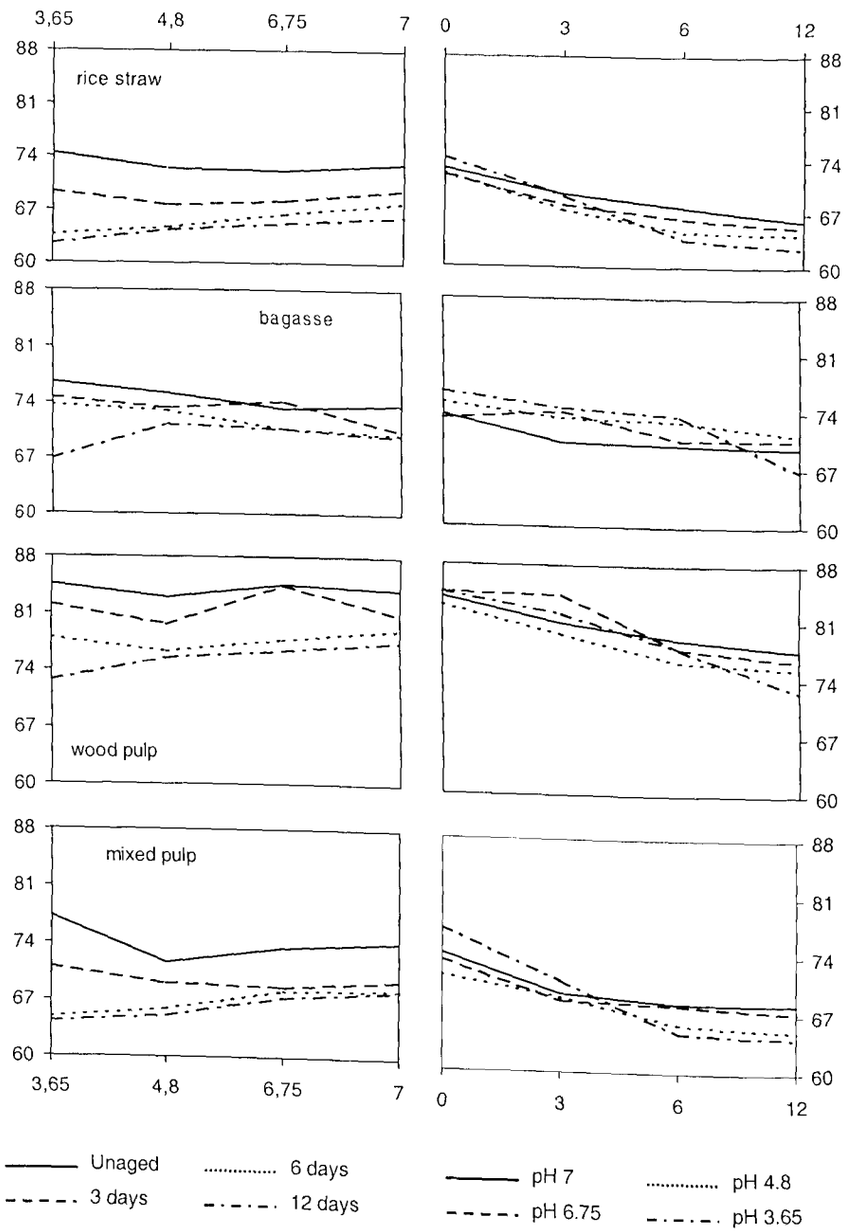

Fig. 4: Relation between the ageing variables (pH: left column; ageing time, *i.e.* days : right column) and brightness (ordinate axis).

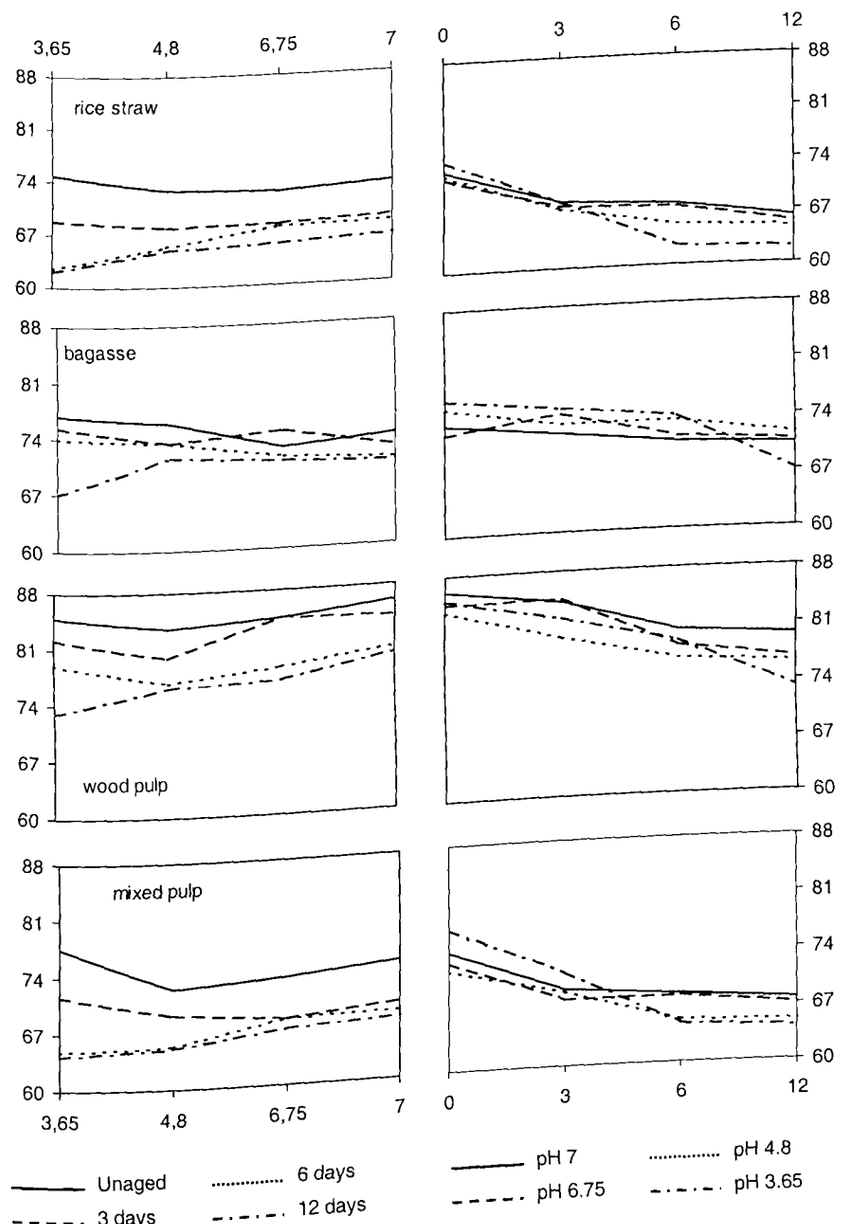

Fig. 5: Relation between the ageing variables (pH: left column; ageing time, i.e. days : right column) and whiteness (ordinate axis).

erally decreased during conventional sizing at pH 4.8. In the paper made from mixed pulp the decrease of α-cellulose was greater than in the papers made from individual pulps reflected by the steeper slope of the lines on the graph.. At constant ageing (left column) α-cellulose slightly increased when the pH of the sizing system was increased from pH 3.65 to pH 6.75 or to pH 7.0, at least with the rice strawpulp (RSP) and bagasse pulp (BP). For the papers containing wood pulp (WP and MP) this increase was significant for pHs higher than 4.8. All papers show the release of free acid as a result of thermal decomposition of aluminium sulfate[21]. The rice straw, bagasse and mixed pulp papers may also have formed carboxyl groups[20] by the oxidation of lignin and hemicellulose during thermal ageing. Both reactions produce high acidity in the paper and consequently increase the degradation of cellulose. This occurs to a greater extent in rice straw, bagasse and mixed pulp papers than in paper made from wood pulp, which is free from lignin and contains less hemicellulose.

For carbonyl content, Fig. 2 shows that, at a constant pH, the formation of carbonyl groups during thermal ageing increased during ageing up to 6 days. Prolonging the thermal ageing to 12 days led to a decrease in the carbonyl content. With constant ageing there is a tendency for the formation of carbonyl groups to decrease, at least at pH levels higher than pH 4.8. It is obvious from the graphs that carbonyl content is at its lowest after the longest period of accelerated ageing. These observations may be explained by the hypothesis that during thermal treatment, in the presence of oxygen, two reactions take place simultaneously: degradation of the cellulose chains and oxidation of the hydroxyl groups. As a result of this latter reaction, carbonyl radicals are formed. During prolonged thermal ageing (12 days), these radicals are cross-link with neighboring carbohydrate chains, which leads to the formation of hemiacetal bonds[21] and to a reduced number of carbonyls. This reaction (cross-linking) involves dehydration, and may be catalyzed by high acidity in the material. Because of this the decrease of carbonyl content in sized paper sheets at pH 7.0 is sometimes lower than acidic sized paper sheets.

Fig. 3 shows that at a constant pH the degree of polymerization (DP) is decreased with longer periods of accelerated ageing, i.e. chain depolymerization is increased with an increased ageing time. The viscosity of cellulose solution is related to the length of the cellulose chains[22]. As with the formation of α-cellulose, the decrease of DP with ongoing ageing time is highest at pH 4.8, for RSP and BP. The slope of all lines in the graphs of the right column of Fig. 3 is steeper with RSP, BP and MP than with WP; this means that the DP of lignin containing pulp is more affected by accelerated ageing than the DP of paper made of lignin free pulp. It can also be observed that the reaction of chain breakage is slowed down after 6 days of accelerated ageing.

Table 6: Kinetic parameters of glycosidic bond cleavage

Paper sample	pH	r	Slope ($k \cdot 10^5$)	Intercept 10^5
Rice straw paper	unsized	0.8743	5.2277	4.060
	3.65	0.9973	5.4714	-1.65
	4.8	0.9211	5.5980	2.80
	6.75	0.9826	4.5980	0.01
	7.0	0.8565	3.3495	11.14
Bagasse paper	unsized	0.9351	3.1940	2.94
	3.65	0.8814	4.0638	3.38
	4.8	0.8947	5.0780	1.50
	6.75	0.9143	2.8666	2.30
	7.0	0.9429	3.8972	6.21
Wood pulp paper	unsized	0.8796	3.5333	6.72
	3.65	0.9798	5.8580	-2.50
	4.8	0.8757	3.5457	2.36
	6.75	0.9042	2.6295	9.22
	7.0	0.9841	1.5447	0.84
Mixed pulp paper	unsized	0.9582	3.8114	4.54
	3.65	0.9595	4.4600	-4.40
	4.8	0.9623	7.1495	-2.32
	6.75	0.8862	5.5895	5.84
	7.0	0.9097	4.2619	2.50

k: rate constant of glycosidic bonds cleavage r: correlation coefficient of the linear relation

Studying the kinetic reaction rate of chain scission, the depolymerization of cellulose during ageing can be considered as a first order reaction[23]. The rate constant (k) for the glycosidic bond breakage was calculated as described in our previous paper[9] and is recorded in Table 6. With the exception of WP the number for slope ($k \cdot 10^5$) is always highest at pH 4.8, which supports the statement already given in interpretation of Fig, 3. That is the acidic preparation (pH 4.8) of lignin containing paper sheets has a higher influence on the degradation rate than with neutral sized paper.

Effect of ageing variables on the optical properties of paper sheets

Regarding brightness and whiteness Figs. 4 and 5 show that both, changing the pH of the sizing system and changing the ageing time, affected the brightness

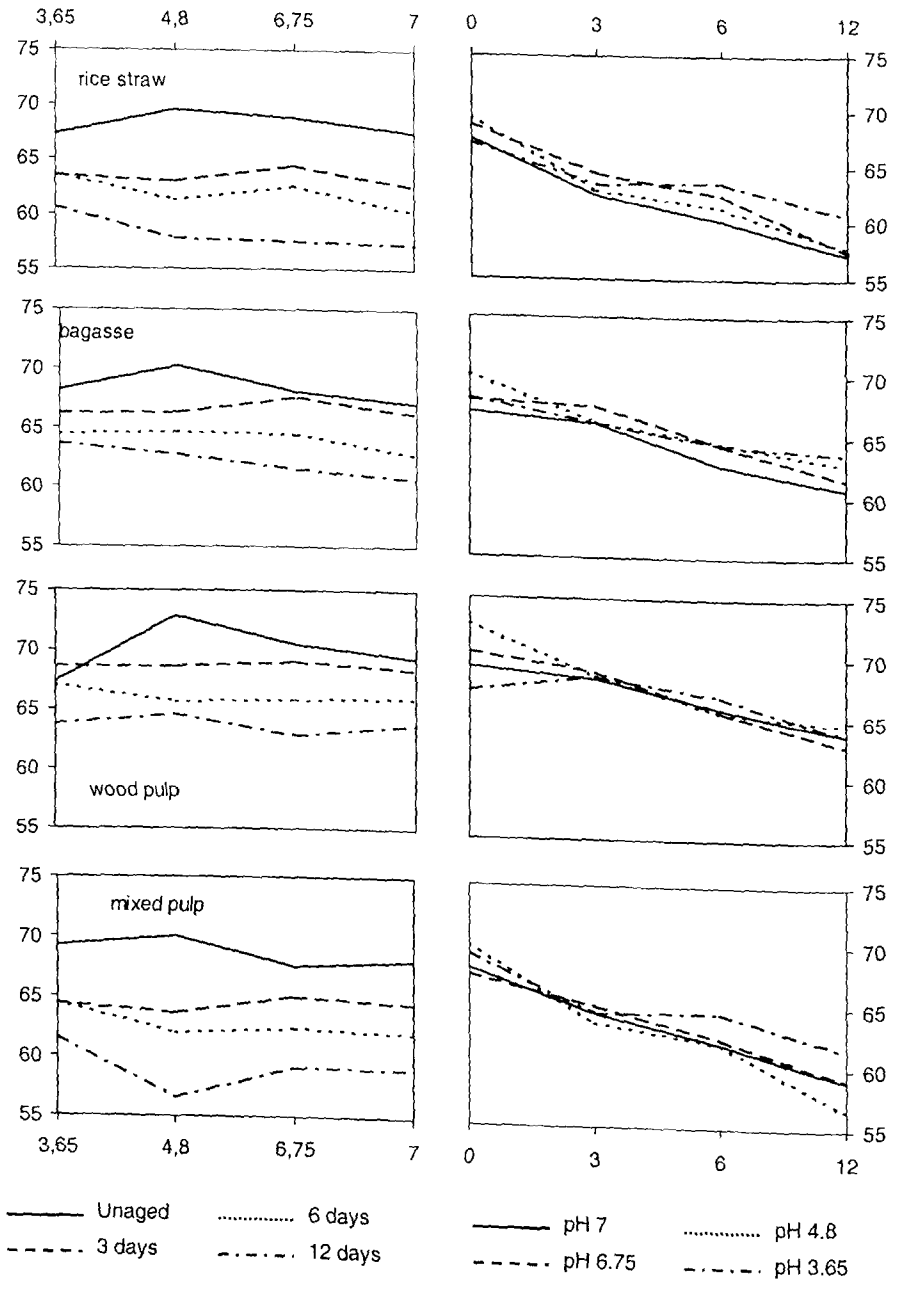

Fig. 6: Relation between the ageing variables (pH: left column; ageing time, i.e. days : right column) and opacity (ordinate axis).

and the whiteness of the paper sheets. The change of these values is higher with rice straw and mixed pulp than with bagasse and, to a lesser extent also wood pulp. This is probably related to the oxidation of lignin containing paper resulting in the formation of additional carbonyl groups. There is an exponential relation between the formation of carbonyl groups of cellulose and its colour[24, 25].

After prolonged thermal ageing the brightness and whiteness decreased in all sizing systems. Increasing the pH from pH 3.65 to pH 6.8 and pH 7.0, i.e., neutral sizing, has a protective effect on brightness and whiteness, at least after longer thermal ageing;, while the pH has little effect on the colour parameters of unaged paper.

Fig. 6 shows that, as with brightness and whiteness, increasing the time of thermal ageing from 0 to 12 days resulted in a gradual decrease in opacity. This is true for all sizing systems by nearly the same amount. The reason for this might be a reduced hygroscopicity as a result of thermal ageing. Additional hydrogen bonds and also chemical bonds are formed, for example, ether linkages between adjacent cellulose molecules[26]. These changes decrease light scattering and reflectance and consequently reduce brightness, whiteness and the amount of light transmitted by paper, i.e. opacity.

The plots of the left column of Fig. 6 and also the numbers in Table 4 show that for unaged paper acidic sizing (pH 4.8) has a positive effect on opacity. This is attributed to the action of alum in settling the fines fraction down, thus a tighter, less porous sheet is obtained. This effect is not stable with prolonged ageing.

Effect of ageing variables on mechanical strength properties of paper sheets

For the number of double folds, the diagram plots in Fig. 7 show that for all sized paper samples the number of double folds decreased with an increasing ageing time. Changing the pH of the sizing system from acidic to neutral, either by decreasing the amount of added alum or adding sodium silicate to the rosin alum system, diminished the loss of double folds, that is giving rise to embrittlement, during thermal ageing. This is related to a decreased amount of acid produced by the hydrolysis of alum in the presence of water; consequently, the depolymerization of cellulose in the presence of heat is diminished[26].From Table 5 it can be seen that optimum response of double folds was noticed at pH 6.75– 7.0 and 3 days. Greatest embrittlement was noticed in all papers at pH 3.65 and after 12 days ageing.

Rasch[2] defines percentages of the double folds after ageing at 100 °C for 3 days, with respect to its value of unaged paper samples as the "permanency fac-

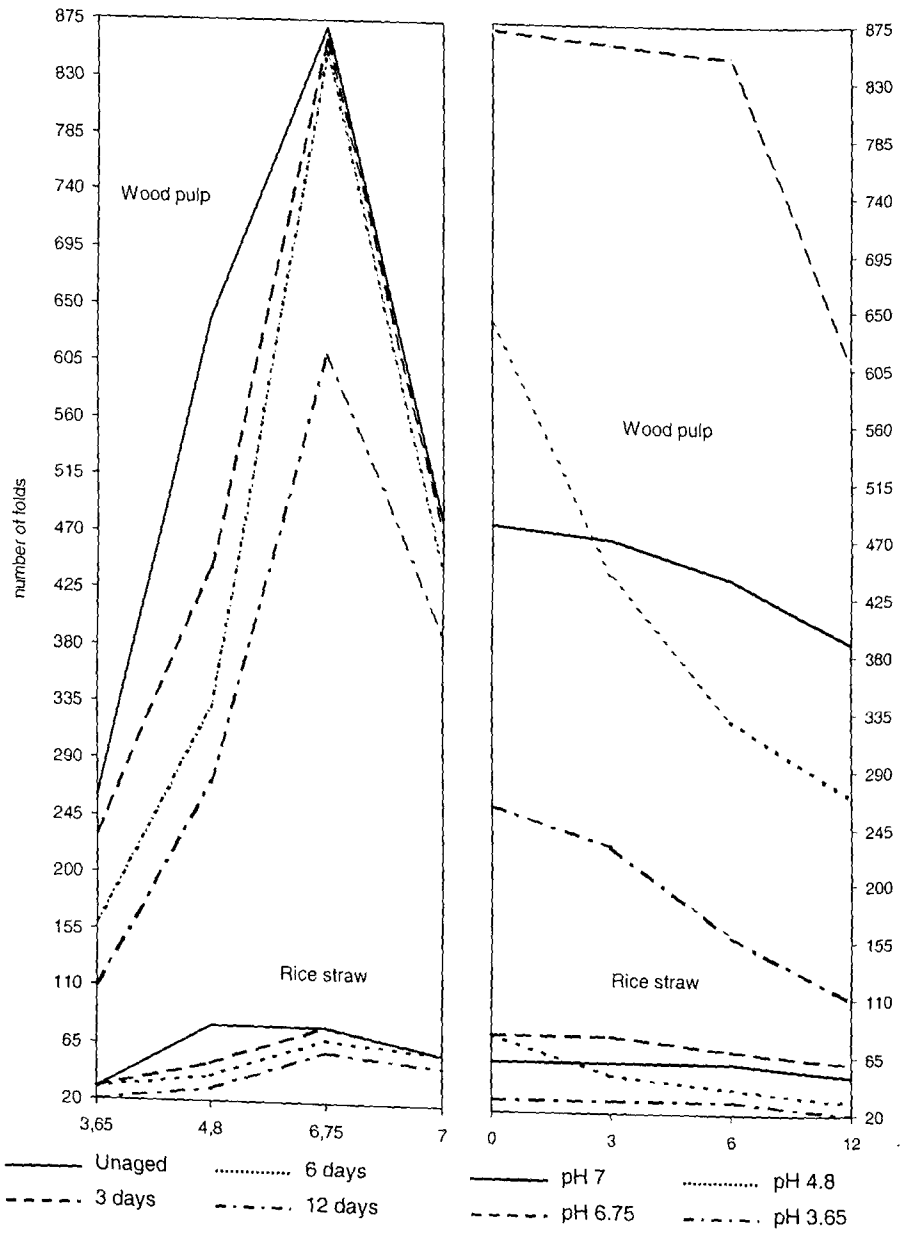

Fig. 7a: Relation between the ageing variables (pH: left column; ageing time, i.e. days: right column) and double fold of rice straw and wood pulp.

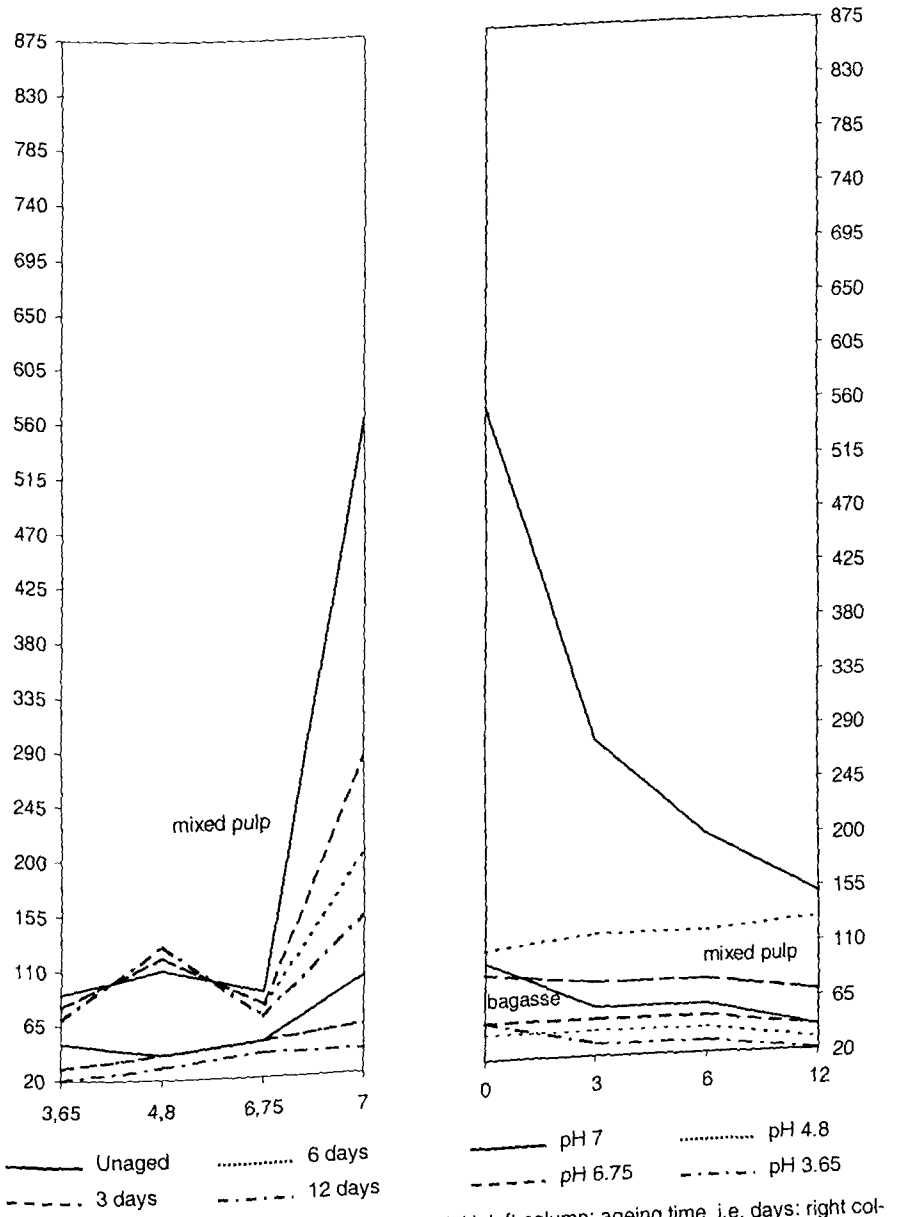

Fig. 7b: Relation between the ageing variables (pH: left column; ageing time, i.e. days: right column) and double fold of bagasse and mixed pulp. NB: For bagasse the plots for 3 days and for 6 days and for mixed pulp the plots for pH 6.75 and for 3.65 are the same.

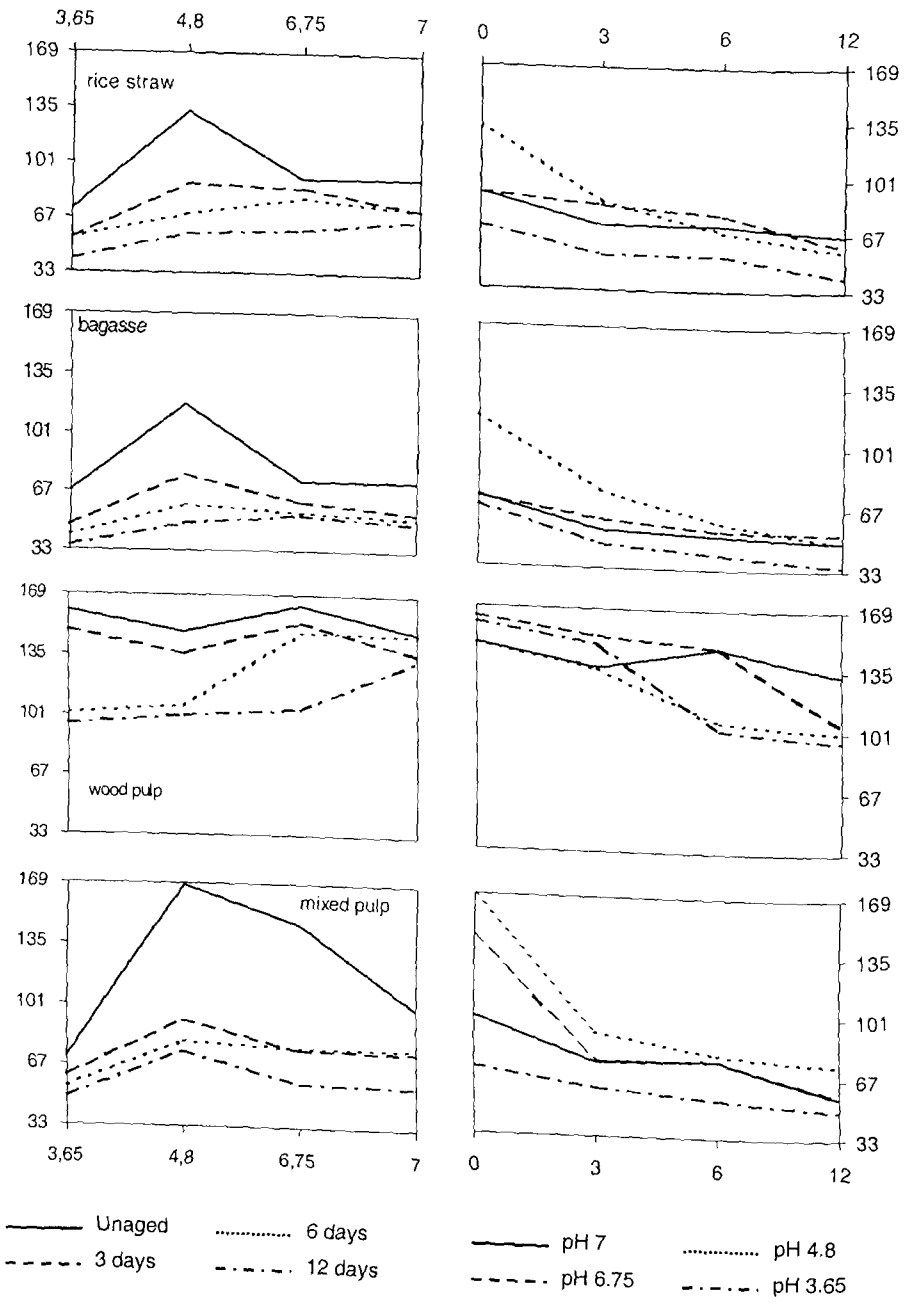

Fig. 8: Relation between the ageing variables (pH: left column; ageing time, i.e. days: right column) and tear factor (ordinate axis).

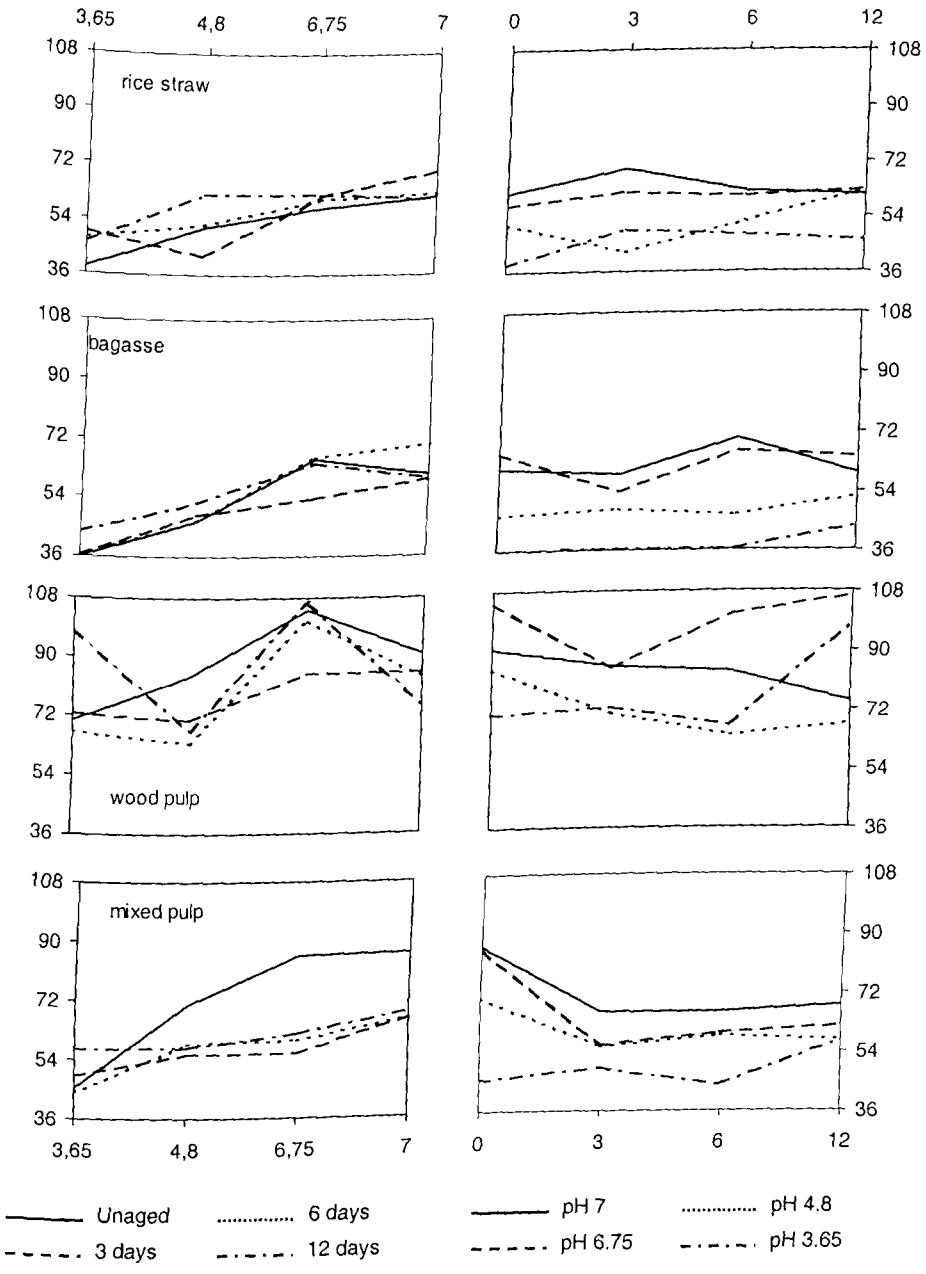

Fig. 9: Relation between the ageing variables (pH: left column; ageing time, i.e. days: right column) and burst factor (ordinate axis).

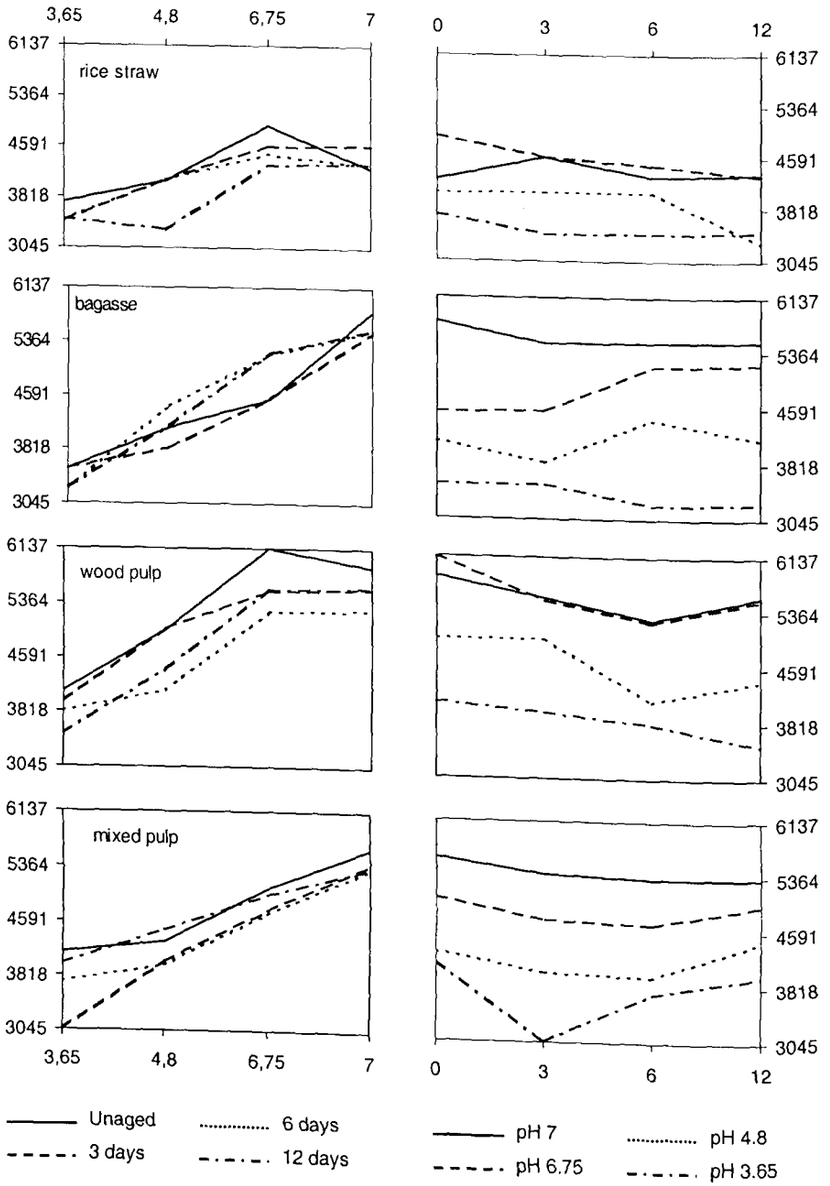

Fig. 10 : Relation between the ageing variables (pH: left column; ageing time, i.e. days: right column) and breaking length (ordinate axis).

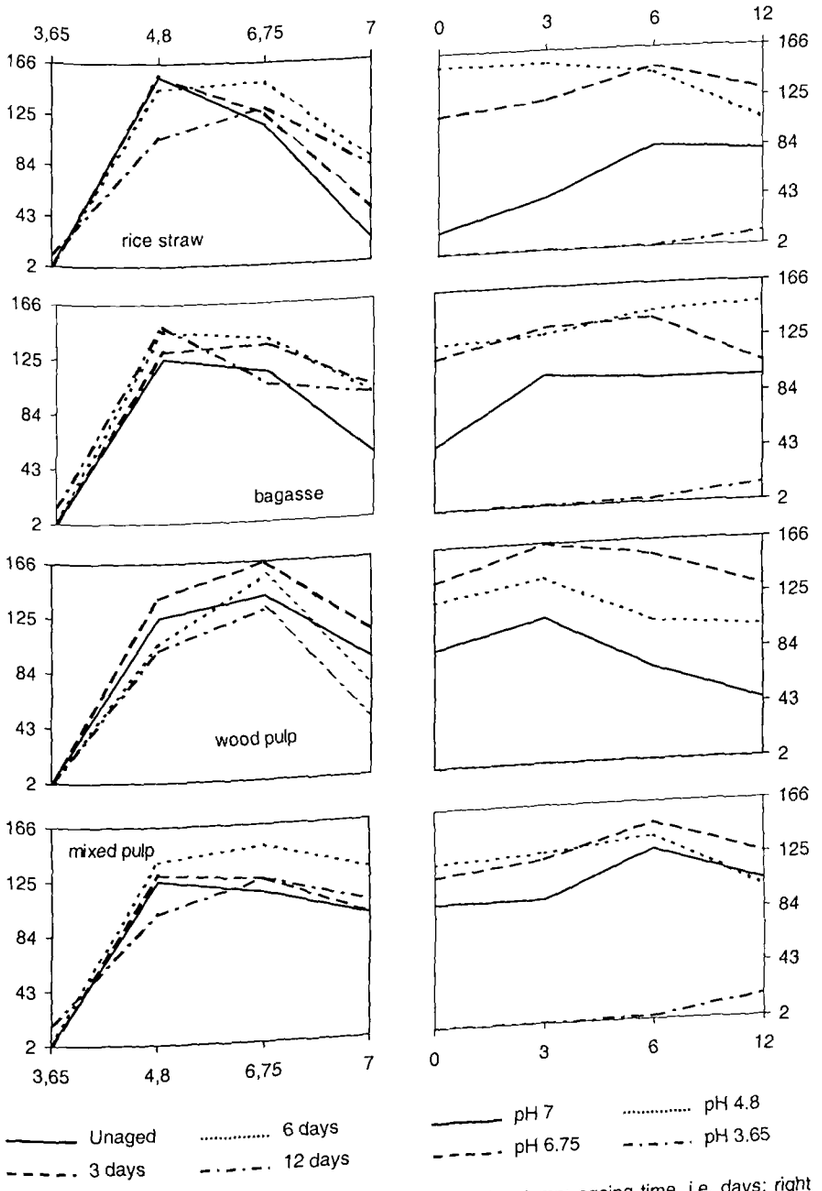

Fig. 11 : Relation between the ageing variables (pH: left column; ageing time, i.e. days: right column) and sizability (ordinate axis).

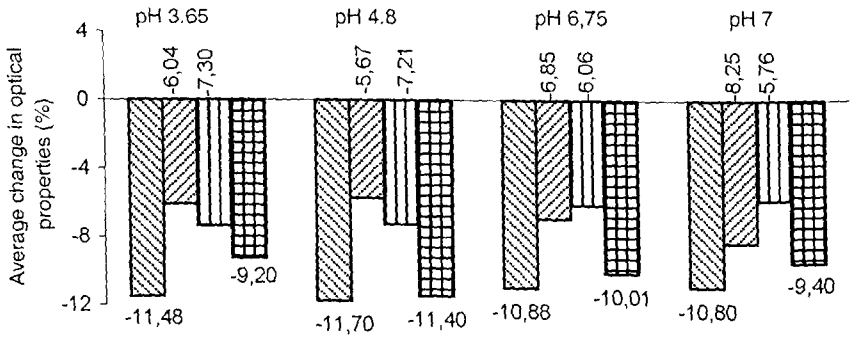

Fig. 12: Average of the percentage changes of the optical properties (brightness, whiteness, opacity) taking place as result of different sizing systems before and after accelerated ageing, in relation to the properties of the unsized and unaged samples (cf. Table 4).

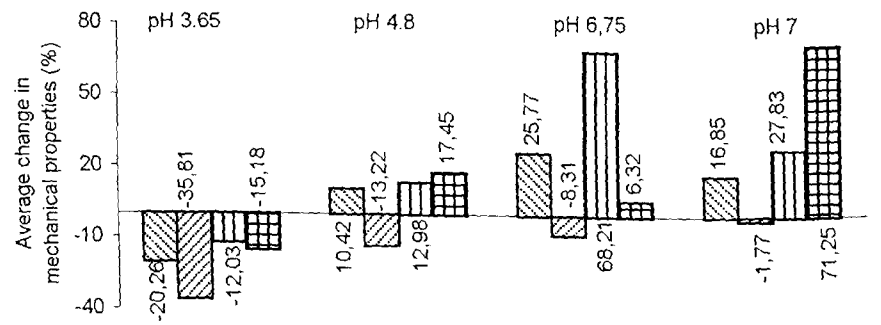

Fig. 13: Average of the percentage changes of the mechanical properties (fold, ear, burst, breaking length) taking place as result of different sizing systems before and after accelerated ageing, in relation to the properties of the unsized and unaged samples (cf. Table 4).

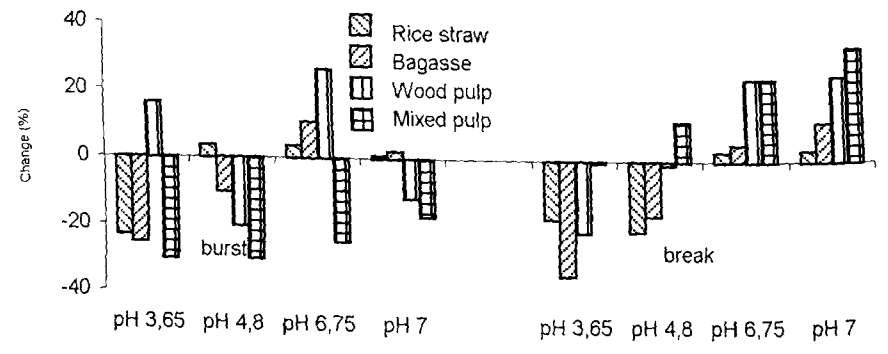

Fig. 14: Percentage change of burst and breaking length after 12 days of accelerated ageing in relation to the unsized and unaged samples (cf. Table 4).

Table 7: Permanency factor, i.e. percentages of the double folds after aging at 100° C for 3 days, with respect to the fold number of unaged paper samples

pH:	3.65	4.8	6.75	7
Rice straw (RSP)	100	62.5	100	100
Bagasse (BP)	60	100	100	60
Wood pulp (WP)	88.5	68.8	98.9	97.9
Mixed pulp)	88.9	109.1	88.9	50

tor". From Table 7 it can be seen that the optimum permanency factor was obtained most frequently at pH 6.75.

From Fig. 8 it can be seen that, for the lignin containing papers the highest tear factor is reached at pH 4.8. This is most clear with the unaged papers and is reduced with ongoing ageing time. Again, for the lignin containing papers, but to a lesser extent also for wood pulp, the sizing at pH 3.65 gave the lowest tear resistance, and, obviously, longer ageing resulted in reduced tear resistance.

Fig. 9 shows that neutral sizing (pH 7/6.75) contributed in providing better burst factor results than acidic sizing. The deleterious effect of rosin/alum system is more apparent with the lignin containing pulps than with the lignin free (cf. Table 1) wood pulp. It may probably be related to the adsorption of a cationic alum-rosin complex on the anionic cellulose fiber which interferes with the hydrogen bonding between the fibers and affects the burst strength of the paper sheets adversely. Optimum ageing variables for paper made from rice straw and mixed pulp are pH 7.0 after 3 days and pH 7/6.75 after 6 days for bagasse and wood pulps (Table 5).

For breaking length Fig. 10 shows that at a constant pH the increase of ageing time is resulted generally in a decrease of breaking length, as with the other mechanical strength properties. There is, however, the exception that in the acidic medium the breaking length of mixed pulp is increased with a longer period of accelerated ageing. This unexpected result may be attributed to the following:

- Thermal auto-crosslinking in cellulose material with the formation of hemiacetal bond[21].
- Prolonged heating time leading to a decrease in sizing efficiency[27].

This hypothesis is emphasized by the decrease of carbonyl content (Fig. 2) and degree of sizability (Fig. 11) after longer ageing.

The distance between different readings and the steepness of the plots in Figs. 7 and 10 indicate that the pH of the sizing system is distinctly more important for

weist, nähern sich den entsprechenden Werten von Papier aus Zellstoff und aus Stoffmischungen, hergestellt unter den gleichen Leimungsbedingungen. Die Ergebnisse lassen es möglich erscheinen, neutralgeleimte Papiere aus einheimischen agrarischen Rohstoffen auch für wichtige Dokumente zu verwenden – freilich unter der Voraussetzung geeigneter Lagerbedingungen in den Archiven.

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the change of double folds and breaking length during accelerated ageing than is the duration of ageing. This is true mainly for paper made from lignin free wood pulp.

The histograms (Figs. 12 and 13) clarify the most suitable permanent paper sheets after thermal ageing for 12 days (≡100 years natural ageing). These histograms show the relationship between the type of pulp and size additives (pH 3.65, pH 4.8, pH 6.75 and pH 7.0) and the average of the total change in optical and mechanical strength properties.

From Figure 12 it is clear that the optical permanence according to the pulp type follows the order:

wood pulp > bagasse pulp > mixed pulp > rice straw pulp

However, the orders of mechanical permanence as shown in Figs. 13 and 14 are:

wood pulp > mixed pulp > rice straw pulp > bagasse pulp.

It seems that low level alum/rosin sized bagasse and rice straw pulp paper can be made, which is resistant to accelerated ageing, if the pH of the sizing system is neutral (pH 7) or nearly neutral (pH 6.75). If we look at the percentage change of burst factor and breaking length of neutral sized paper sheet aged for 12 days it can even be said that these pulps are comparable to wood pulp paper, insofar as the change values are positive (break) or even better (burst). From the above results we can recommend that neutral sized paper sheets from local agricultural wastes can be used even for important documents – as long as recognised, suitable environmental conditions within an archive are maintained.

SUMMARIES

The correlation between the permanence of paper made from straw pulps and ageing variables

Paper sheets from local Egyptian straw pulps (bleached soda rice straw- and kraft bagasse) were prepared. Different ageing variables, namely: pH of sizing system (3.65 –7.0) and time of accelerated ageing (0 – 12 days) were studied. The effects of pH and time of ageing on the chemical, optical and mechanical properties were correlated and compared with samples prepared from imported bleached wood pulp (kraft softwood) and its blend with a local pulp. The results show that both pH of the sizing system and time of ageing are important for paper permanence. Relatively high permanent paper sheets were obtained from low level alum/rosin-sized bagasse pulp (pH 6.75) and sodium silicate-alum/rosin sized rice straw pulp (pH 7.0), i.e. by neutral sizing. Breaking length and burst factor of such a paper after 12 days ageing are comparable to the values of sheets made from wood and from mixed pulps under the same ageing variables. The results recommend the use of neutral sized paper from local agricultural wastes even for important documents – assuming appropriate environmental conditions are maintained.

La relation entre la permanence du papier fabriqué à partir de pâte de paille et les variables déterminant son vieillissement

Des feuilles de papier de production locale égyptienne à base de pâte de paille (paille de riz blanchie à la soude et kraft bagasse) ont été utilisées. Les différentes variables entraînant une détérioration de la qualité ont été étudiées, à savoir le pH du système de collage (3,65 – 7.0) ainsi que la durée du vieillissement accéléré (0 - 12 jours). Les effets du pH et de la durée du vieillissement sur les propriétés chimiques, optiques et mécaniques ont été mis en corrélation et comparés aux qualités des échantillons préparés à base de cellulose blanchie importée et au mélange de celle-ci avec la pâte locale. Les résultats obtenus démontrent que le pH du système de collage ainsi que la durée du vieillissement sont tous les deux déterminants pour la permanence du papier. On a obtenu à partir d'un mélange local de moindre qualité fait à base de bagasse (pH 6,75, tige de canne à sucre) avec collage de résine et d'alun des feuilles dont la permanence du papier était relativement élevée. Les résultats obtenus mettent en évidence que le pH du système de collage ainsi que la durée du vieillissement sont tous les deux déterminants pour la permanence du papier. On a obtenu des feuilles dont le niveau de permamence du papier était relativement élevé qui étaient fabriquées à partir d'un mélange local de moindre qualité fait à base de bagasse (tige de canne à sucre) d'un pH de 6,75 avec collage de résine et d'alun et d'une pâte de paille de riz avec collage de résine et d'alun au silicate de sodium avec un pH de 7,0 , c'est-à-dire avec un collage neutre. La longueur de rupture et la pression d'éclatement que présente ce papier après 12 jours de vieillissement sont comparables aux valeurs correspondantes des feuilles de papier à base de cellulose et de mélanges de matériaux fabriqué sous les mêmes conditions de collage. Ces résultats permettent de recommander l'utilisation de papier émanant des produits agraires locaux avec collage neutre, même pour les documents importants, si évidemment les conditions appropriées de stockage des archives sont garanties.

Das Verhältnis zwischen der Dauerhaftigkeit von Papier aus Strohstoff und seinen die Alterung bestimmenden Variablen

Es wurden Probeblätter aus einheimischem ägyptischem Strohstoff (Soda-Reisstroh und Kraft-Bagasse, gebleicht) hergestellt. Die beiden Variablen, welche die Qualität beeinflussen, nämlich pH des Leimungssystems (3.65–7) und Dauer einer beschleunigten Alterung (0–12 Tage) wurden untersucht, d.h. ihr Einfluß auf die chemischen, optischen und mechanischen Eigenschaften wurden in Beziehung gesetzt und verglichen mit eben diesen Eigenschaften von Papier, das aus importiertem Zellstoff und aus Mischungen desselben mit den einheimischen Stoffen hergestellt worden war. Die Ergebnisse zeigen, daß sowohl das pH des Leimungssystems als auch die Alterungszeit von Bedeutung für die Dauerhaftigkeit sind. Als relativ dauerhaft erwiesen sich die aus geringwertigem einheimischem Bagasse-Stoff unter Harz-Alaun-Leimung bei pH 6.75 und aus Reisstroh-Stoff unter Natriumsilikat-Harz-Alaun-Leimung bei pH 7.0 hergestellten Papiere, d.h. bei Neutralleimung. Reißlänge und Berstdruck, die solches Papier nach 12 Tagen Alterung auf-

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