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Hydrolytic and Oxidative Degradation of Paper

by SIMONA MARGUTTI, GIUSEPPINA CONIO, PAOLO CALVINI & ENRICO PEDEMONTE

INTRODUCTION

It is well known that cellulose is the main component of paper. In order to analyse paper degradation therefore it is necessary to study the degradation mechanisms of cellulose.

Cellulose is a non-branched polymer of glucose linked through 1,4-β-glucosidic bonds (Fig. 1). The number of units is variable and constitutes the degree of polymerisation (DP); its value depends on the nature of the plant from which the cellulose is extracted and on the type of treatment during the extraction process.

The principal changes that act in the structure of cellulose and that cause its alteration are:

- biodegradation,
- photodegradation,
- acid hydrolysis,
- oxidation.

A complete analysis of cellulosic material is quite complex because these phenomena are all related to each other[1]. In this study we consider only oxidation, with the intention of reproducing natural oxidation ageing and to cause/encourage a coupling reaction of the oxidation products. A better understanding of degradation processes is a prerequisite for restoration procedures.

The oxidation reactions of cellulose involve the primary and secondary hydroxy groups of the pyranose ring and result in carbonyl and carboxyl groups. These groups are able to absorb visible radiation; they are chromophores and as such are responsible for the yellowing of paper. The oxidation reaction can be, but is not necessarily, accompanied by the opening the pyranose ring (Figs. 2 and 3). In both cases the glucosidic bond becomes weaker; the formation of carboxyl groups increases acidity and induces depolymerisation (Fig. 4), thus reducing the physical and mechanical strength of the material.

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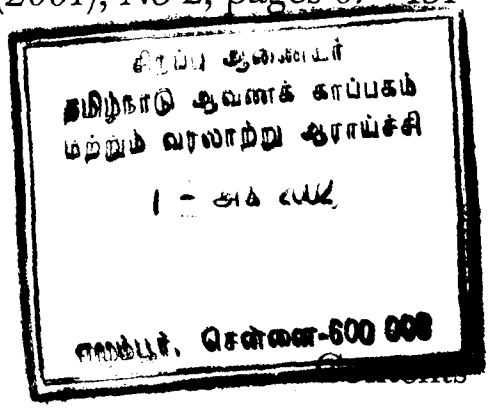

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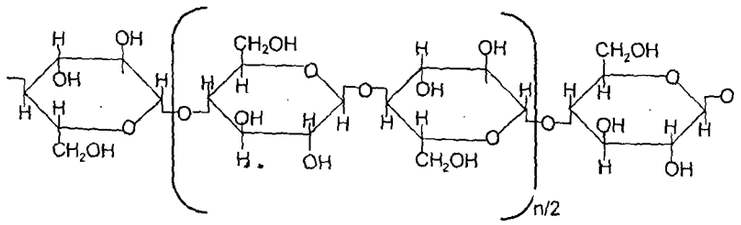

Fig. 1: The structure of cellulose: poly[β-(1,4)-D-glucopiranose].

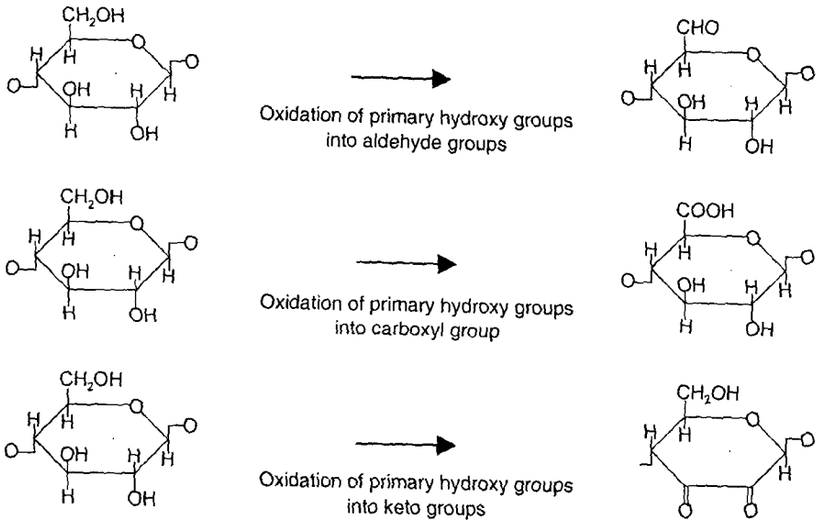

Fig. 2: Main oxidation reactions of the cellulose molecule without opening of the pyranose ring

EXPERIMENTAL

Materials

The cellulose substrate used for the experiment was a Whatman no. 1 filter paper; this type of paper is obtained from cotton linters and can be considered to be pure cellulose. Parallel tests were done with cellulose for chromatographic use (Sigma-Aldrich 6288), in order to compare the results of oxidation degradation on samples of different chain length. The DP of Whatman no. 1 is 1230, that of Sigma-Aldrich 6288 is 184.

The use of these samples for our research could be considered as an unreasonable simplification as, in general, paper does not consist of just pure cellulose, it is

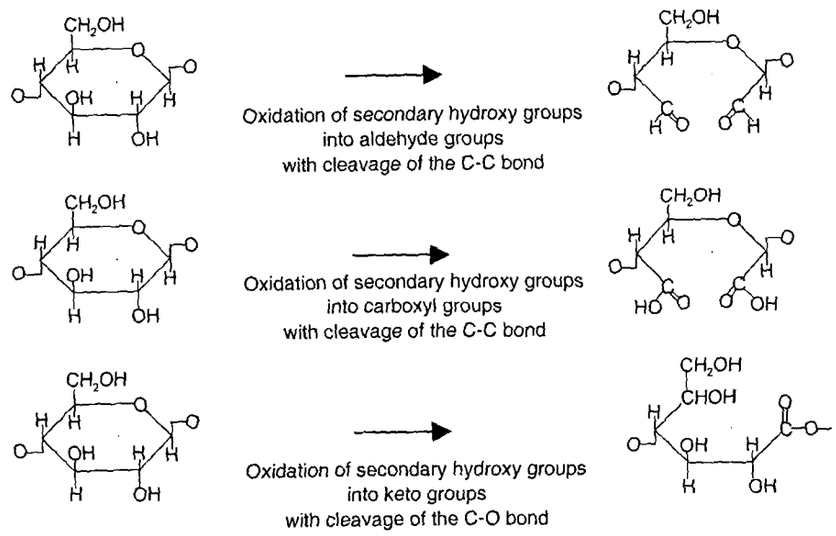

Fig. 3: Main oxidation reactions of the cellulose molecule with opening of the pyranose ring.

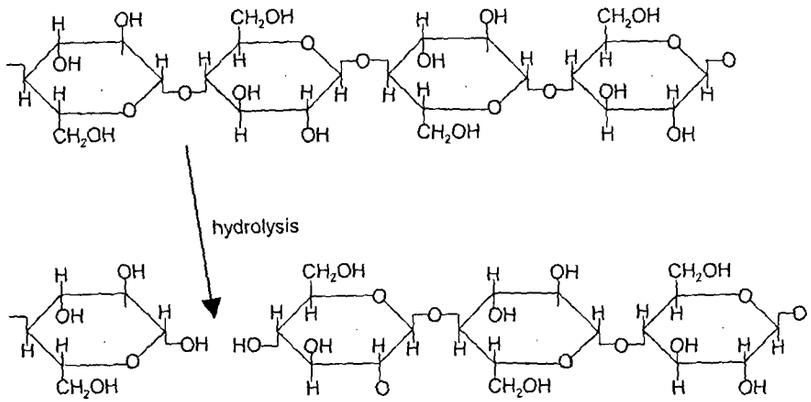

Fig. 4: Hydrolysis reaction of the β-(1,4)-D-glucosidic bond.

a heterogeneous and quite complex material, usually a mixture of fibres of vegetable origin, of minerals, organic sizing agents and chemical additives of different natures. Cellulose is the main component of fibres that also contain lignin and hemicellulose. Despite these considerations, we decided to work on pure cellulose only, in order to eliminate interference from extraneous substances. This

Table 1: Functional groups formed after oxidation with hypochlorite, depending on pH.

pH < 7.5	7.5 < pH < 8.5	pH > 8.5
CO	CHO	COOH
CHO	CO	CHO
COOH	COOH	CO

enabled us to study the oxidation process with different oxidizing agents on a particular, simple system.

Previous studies have brought up the distinction between *specific* and *non-specific* oxidizing agents. In this study samples were treated with sodium hypochlorite (NaClO) and sodium metaperiodate ($NaIO_4$)[2,3] in order to study the two different types of oxidation.

Hypochlorite is an oxidizing agent, characterized by a non-specific action. It was chosen because it is commonly used in paper conservation for bleaching. Sodium hypochlorite produces a *random oxidation*, that is it does not preferentially attack a certain position of the pyranose ring; also the nature of the functional groups produced by oxidation is heterogeneous, they depend on the reaction conditions of temperature and pH. Ignoring the kinetic effect of temperature, during oxidation with hypochlorite, the ratio between the carboxyl and carbonyl groups varies depending on the pH. Under highly alkaline conditions carboxyl groups are preferentially formed, at slightly alkaline or acid pH carbonyl groups prevail.

As shown in Table 1, it is possible to isolate three different ranges of pH; in each of them the formation of a preferential functional group is observed. For pH values below 8.5 carbonyl groups prevail; for values between 8.5 and 7.5 aldehyde groups are predominant, whereas under pH 7.5 keto groups predominate. Raising the pH, the formation of carboxyl groups is observed; in a strongly alkaline medium (pH > 10) the formation of carbonyl groups, especially of ketones, is negligible.

Oxidation with hypochlorite was carried out at three different pH values, 5, 8, 12. These were chosen in order to replicate the three possible circumstances of a majority of keto groups (pH = 5), a majority of aldehyde groups (pH = 8) and a majority of carboxyl groups (pH = 12). Considering the specific oxidizing agent, we decided to use the Malaprade reaction, that is to employ sodium metaperiodate. Its point of attack is the C2–C3 bond and it involves the formation of a dialdehyde[4,5] (Fig. 5).

Sodium hypochlorite (3% of active chlorine) and sodium metaperiodate p.a. (99.8%) from Sigma-Aldrich were used without further purification.

Together with oxidative treatments, acid treatment was also carried out, using commercially available hydrochloric acid.

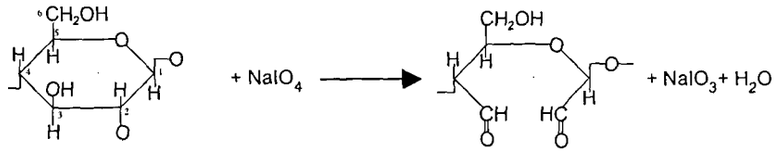

Fig. 5: Oxidation with sodium metaperiodate

The viscosity measurements were carried out in cuproethylendiamine (CED) using a commercially available product.

TREATMENTS

Oxidations

In all of the treatments the sample/solution ratio was 1g/100ml. Oxidation was carried out at 25°C on dry samples, which measured 1 x 2 cm and which were of constant weight for different lengths of time (cf. Tables 3 and 4). The oxidized samples were dried and kept in a sample holder in the dark.

Oxidation with metaperiodate was done with solutions of the stoichiometric quantities of the salt in deionized water. For oxidation with hypochlorite the different pH values 8 and 5 were adjusted with acetic acid (commercially available, 99.8% pure). For pH 12 no buffer was required. In all cases the pH of the solution was constant during the whole process.

All oxidation treatments were done in closed vessels and were stirred continuously. After treatment the samples were washed with deionized water up to neutrality.

Two acid treatments were used.

- Half the samples treated as described above were dried and then dipped for 2.5 h into hydrochloric acid solution. The ratio between the sample and the hydrochloric acid solution was 1 g/100 ml.
- Half the samples were exposed for 96 h to the acid vapour in a desiccator.

In both cases all of the samples were washed after the acid treatment and dried until no appreciable variation of their weight was observed.

Viscosity measurements

Measuring the degree of polymerisation (DP) can be done using direct methods based on physical-chemical properties. However, this type of approach requires

complex procedures and equipment and is therefore not suitable for routine measurements. Instead, a non-direct measurement, such as measuring viscosity, is more suited for an everyday application and is widely used in paper conservation research.

Viscosity is related to DP by an empirical relationship known as the Mark-Houwink-Sakurada equation that is generally expressed as:

$$DP = K[\eta]^a$$

K and a are experimental constants. [η] is the *intrinsic viscosity* that is dependant on the molecular mass only and is independent from the viscosity of the solvent, from the concentration of the polymer and from the type of viscosimeter. In the work presented here, this method was applied to the artificially aged, oxidised samples of cellulose in order to evaluate and compare the action of the different oxidising agents.

When testing cellulose using the viscosity method there are several different calibrations because there are many values for K and a, which, quite often are not in agreement. The main reason for the discrepancies derives from the difficulties of applying direct methods on such a complex polymer as cellulose. Another reason for different values for K and a given in the technical literature may be differences in methods of measuring the intrinsic viscosity. Cellulose, causes therefore, unusual problems even in the application of a relatively simple technique such as measuring viscosity.

The specific solvent for measuring DP of cellulose is cuproethylendiamine (CED). It has been used for this research because it allows the easier and more immediate preparation of cellulose solutions. The values for K and a were those indicated in the UNITEX CH 33[6] project: K = 1.5; a = 1. Thus, from the values of $[\eta]^{25}$, expressed in ml/g, the DP has been calculated as

$$DP = 1.5\ [\eta]^1$$

The viscosity measurements were performed at 25°C using 0.5 M aqueous solution of cuproethylendiamine in an Hubbelohde viscometer. The dry samples were weighed and treated with CED in a closed vessel under a nitrogen atmosphere and were stirred continuously. The solution must be prepared in the absence of oxygen because oxygen has a rapid degrading effect on the polysaccharide solution.

Infrared spectroscopy in Fourier transform

Vibrational spectroscopy has been, for many years, one of the mostly commonly used experimental techniques for the characterization of materials, both in research laboratories and in industry[7]. During the last decades infrared spectroscopy has also been used quite often to solve analytical problems in the field of cultural heritage, especially since instruments with a high signal/noise ratio have become commercially available. These instruments are able to measure very weak signals in a short time so that only a very little material is necessary for qualitative results, this means for instance that samples can be taken from art works and from objects of historical and cultural interest[8].

Reflection and transmission are the two principal types of analysis used in FTIR spectroscopy. The instrument used for work reported here is a FTIR Brucker IFS 66 spectrometer with a Globar source (silicon carbide brought up to incandescence), with a water cooling system and OPUS data processing program. The samples have been analysed for transmission measurements, i.e. by registering their absorbance. Transmission measurements vary depending on the state of the sample[9]. In the work reported here measurements were made on solid samples that were dispersed in a 13 mm potassium bromide (KBr) disk of variable depth (between 0.1 and 1 mm).

Preparing the disks is the most delicate phase; in fact the results of the analysis depend on how this operation has been carried out. The samples must be accurately "stripped", so that the appearance of the paper becomes similar to that of cotton. The KBr must be ground prior to use in a ball grinder and kept in a dessicator. Cellulose and KBr were then transferred to an oven and kept there for 24 hours at 90°C under a dynamic vacuum. At the end of the thermal treatment, the cellulose was mixed with KBr in a 1:500 ratio and ground in an agate mortar until a fine powder, which was as even as possible, was obtained. It is necessary to make the samples as small as possible to minimize the scattering effects of the incident radiation that is often the main drawback of this type of analysis. From Rayleigh's relationship:

$$S \propto d^3\nu^4$$

scattering increases with rising frequencies (ν) and with the dimensions of the particles (d); for IR they should have a diameter in the order of μm. The grinding procedure must be done as quickly as possible because prolonged exposure of the sample to humidity (present in the surrounding air) would nullify the previous vacuum treatment. After the samples have been mixed they are transferred again to the oven and kept for 24 h under the previously described conditions. Finally, the disk is prepared by using a press connected to a vacuum pump, it is also necessary in this phase to avoid exposing the sample to humidity.

Cellulose is highly hygroscopic; the water content of Whatman no. 1 under normal laboratory conditions is ca. 5%. In the IR spectrum this is confirmed by a peak between 1635–1670 cm^{-1} that can be very broad and cover the peaks of the

Table 2: Viscosity measurements of the non treated samples. $[\eta]^{25}_{CED\ 0.5}$ = intrinsic viscosity at 25°C in 0.5 M CED; - DP_{unitex} = mean viscosimetric polymerisation grade.

Sample	Viscosity $[\eta]^{25}_{CED\ 0.5}$ (dl/g)	DP_{unitex}
Whatman No.1	8.2	1230
Sigma-Aldrich	1.22	184

carbonyl groups of the cellulose samples. Comparing the spectra of disks, freshly prepared according to the previously described procedure, with those of the same disks kept in a dessicator for a month, we observed significant differences in two regions of the spectrum. That around 1640 cm^{-1} corresponded to the absorption of water, and that around 3400 cm^{-1} was related to the stretching of the hydroxy groups. Nevertheless the absorption of water did not alter the absorption capabilities of the sample; in fact, the spectrum was the same except for these two modifications.

Finally, we emphasise that it is of crucial importance to prepare correctly the KBr disk in order to estimate the absorption capabilities of the sample in the region of the carbonyl groups.

Results

The samples of Whatman filter paper no. 1 and of Sigma-Aldrich 6288 cellulose for chromatographic use were treated with sodium hypochlorite (NaClO) and sodium metaperiodate ($NaIO_4$) for different lengths of time. Viscosity measurements were used to estimate the effects of the treatments on the polymerisation grade. Table 2 gives the viscosity measurements of the original samples.

Oxidation with sodium hypochlorite

Table 3 shows the viscosity and DP of Whatman no. 1 paper oxidized with hypochlorite at three different pH values obtained with the Mark-Houwink-Sakurada equation. Fig. 6a gives the decrease of DP. The curves at the three different pH values have a similar shape; in the first section, the DP values decrease rapidly, afterwards the depolymerisation process slows down until a nearly constant value is reached. It is evident that the pH of the oxidizing system affects the speed of the degradation process. If oxidation occurs in an acid medium (pH 5), the minimum value of DP an be reached in an hour, the hydrolysis of the glucosidic bond

Table 3: Viscosity ($[\eta]^{25}_{CED\ 0.5}$; (dl/g) and DP of Whatman no. 1 filter paper oxidized by NaClO.

	pH5		pH8		pH12	
$t_{oxidation}$ (hours)	viscosity	DP	viscosity	DP	viscosity	DP
0	8.2	1230	8.2	1230	8.2	1230
1	1.00	150	5.1	770	4.7	713
2.5	0.82	123	3.0	450	2.4	360
3.75	0.80	120	2.6	400	2.2	330
5	0.76	115	2.3	350	2.0	300
24	0.73	110	1.6	250	1.3	190
48	0.72	109	1.2	160	1	150

Table 4: Whatman No. 1 paper treated with hydrochloric acid.

ph	$t_{oxidation}$ (hours)	Viscosity $[\eta]^{25}_{CED\ 0.5}$ (dl/g)	DP_{unitex}
5	2.50	8.16	1225
0.7	2.50	6.1	915
0.7	96	4.5	675

is speeded up by a high concentration of hydrogen ions. In an alkaline medium the degradation is slower. Comparing the curves of oxidation at pH 8 and 12 it becomes evident that, at the higher pH, DP also decreases more rapidly, implying that an alkaline medium also has a catalytic action on the hydrolysis of the glucosidic bond. With an increased oxidation time the three curves converged to the same value. This means that the pH had only a kinetic effect on the decrease of DP. Depolymerisation was not only influenced by the pH but also by the oxidizing effect of hypochlorite. As mentioned above, the possible points of attack of a non-specific oxidizing agent such as hypochlorite, are the C_6, C_2 and C_3 bonds, and, as a consequence, also the atoms C_1 and C_4 are involved. The presence of oxidized functional groups at carbon atoms adjacent to an atom involved in the glucosidic bond affects its stability, that is it increases its sensitivity to hydrolysis.

In order to evaluate the effect of acidity on the depolymerisation process, Whatman paper no. 1 was treated with hydrochloric acid. The viscosity data are listed in Table 4. The effect of this acid treatment is less pronounced than the combined effect of the acidity and the oxidation. Comparing the DP after 2.5 hours of treatment at pH 5 (Table 4) with that after hypochlorite oxidation for the same time and at the same pH (Table 3), a decrease to 1225 can be seen in the first (HCl) and to 123 in the latter case (NaClO), that is degradation is ten times more. The data confirm the symbiotic action of oxidation and of acidity on the depolymerisation process.

Table 5: Viscosity ($[\eta]^{25}_{CED\ 0.5}$; (dl/g) and DP of Sigma-Aldrich 6288 cellulose oxidised by NaClO.

	pH5		pH8		pH12	
$t_{oxidation}$ (hours)	viscosity	DP	viscosity	DP	viscosity	DP
0	8.2	184	1.20	184	1.20	184
1	4.7	137	1.17	176	1.13	170
2.5	2.4	114	1.11	167	1.01	152
3.75	2.2	108	1.04	157	0.97	146
5	2.0	107	1.00	150	0.92	138
24	1.3	106	0.90	136	0.81	122
48	1	104	0.79	119	0.75	113

Table 6: Sigma-Aldrich 6288 cellulose treated with hydrochloric acid.

ph	$t_{oxidation}$ (hours)	Viscosity $[\eta]^{25}_{CED\ 0.5}$ (dl/g)	DP_{unitex}
5	2.50	1.22	183
0.7	2.50	1.18	178
0.7	96	1.13	170

Table 7: Viscosity data of the oxidation by NaClO for two weeks (336 hours).

pH (NaClO)	Viscosity $[\eta]^{25}_{CED\ 0.5}$ (dl/g)	DP_{unitex}
5	0.72	109
8	0.73	111
12	0.72	109

Table 8: Viscosity ($[\eta]^{25}_{CED\ 0.5}$; (dl/g) and DP of Whatman no. 1 paper oxidised by $NaIO_4$.

	0.01 M		0.03 M		0.1 M	
$t_{oxidation}$ (hours)	viscosity	DP	viscosity	DP	viscosity	DP
0	8.20	1230	8.20	1230	8.20	1230
1	5.93	890	3.06	460	1.60	241
2.5	2.60	390	1.95	293	1.23	185
3.75	2.20	330	1.66	250	1.13	170
5	2.00	300	1.60	240	1.10	165
24	1.60	250	1.42	214	1.07	160
48	1.46	240	1.40	210	1.07	160

Similar results were obtained with Sigma-Aldrich 6288 cellulose samples for chromatographic use. The experimental data are listed in Table 5 and Fig. 6b. The curves were very similar to those of the Whatman no. 1 samples; this led to

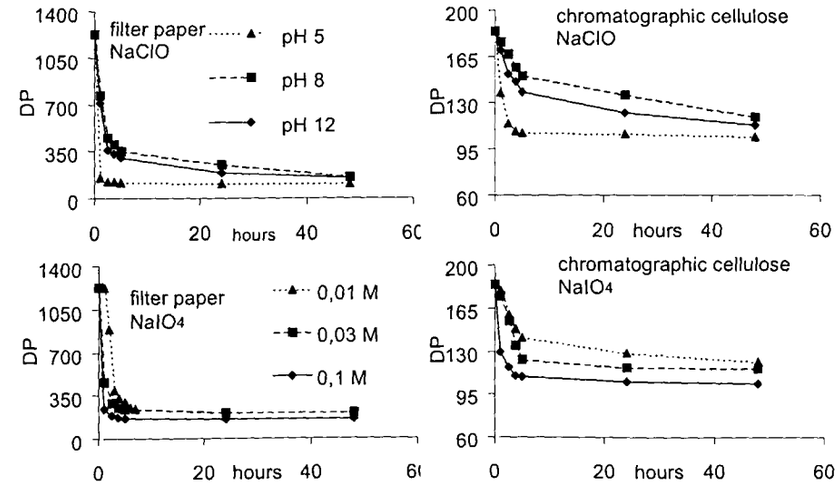

Fig. 6: Decrease of DP vs oxidation time of Whatman no. 1 filter paper (left column) and of Sigma-Aldrich 6288 cellulose (right column), with hypochlorite at different pH (first row) and with sodium periodate in different concentration (second row).

the conclusion that the results depended on the oxidizing system and not on the kind of sample.

The data of depolymerisation of Sigma-Aldrich 6288 cellulose induced by the hydrochloric acid treatments are given in Table 6. Comparing them with the data of Table 4 it became obvious that the relative reducing rate was smaller than that of Whatman paper under the same conditions.

Our study of oxidation with hypochlorite was completed by submitting the samples to prolonged oxidation increasing exposure for up to two weeks (336 hours) (Table 7). We observed that the DP for both kinds of samples, irrespective of the pH value did not drop below 109. This is the value of the complete degradation of cellulose caused by a treatment with hypochlorite.

Oxidation with sodium metaperiodate

We studied the degradation of cellulose oxidized by aqueous solutions of metaperiodate at different concentrations: 0.01 M, 0.03 M and 0.1 M. These solutions were slightly acid with a pH of 5.4–5.7 for the more diluted and 4.7 for the more concentrated solutions. Table 8 shows viscosity data and DP, Fig. 6c and Fig. 6d show the average DP vs. oxidation time. It can be seen that by increasing the

Table 9: Comparison between 2.5 hours oxidation with metaperiodate and 2.5 hours treatment with hydrochloric acid.

treatment	pH	DP
HCl	5	1225
HCl	0.7	915
$NaIO_4$ 0.01M	5.7	390
$NaIO_4$0.03M	5.4	293
$NaIO_4$0.1M	4.7	185

Table 10: Viscosity ($[\eta]^{25}_{CED\ 0.5}$; (dl/g) and DP of Sigma-Aldrich 6288 cellulose oxidised by $NaIO_4$.

	0,01 M		0,03 M		0,1 M	
$t_{oxidation}$ (hours)	viscosity	DP	viscosity	DP	viscosity	DP
0	1,23	184	1,23	184	1.23	184
1	1,20	180	1,16	175	0.86	130
2,5	1,06	160	1,03	155	0.78	117
3,75	0,98	148	0,90	135	0.73	110
5	0,94	141	0,82	123	0.72	109
24	0,86	129	0,78	117	0.70	105
48	0,81	122	0,77	116	0.69	104

Table 11: DP of the Whatman no. 1 paper and of the Sigma-Aldrich 6288 cellulose after oxidation (336 hours) with $NaIO_4$.

$NaIO_4$	Whatman no. 1	Sigma-Aldrich 6288
0.01M	110	109
0.03M	109	105
0.1M	109	105

concentration of the oxidizing agent, DP decreased faster; nevertheless the three curves converged to a common final number that corresponded to complete degradation. The shape of the curves was similar to that produced by the oxidation with hypochlorite, although the depolymerisation curve was somewhat smaller. As said above, metaperiodate does not act directly on the glucosidic bond, but attacks only the link between carbons 2 and 3 of the pyranose ring. The depolymerisation observed in metaperiodate oxidized cellulose was therefore the combined effect of acidity and the presence of aldehyde in the ring. Comparing these data with those of the treatment with hydrochloric acid, we concluded that depolymerisation occurring after treatment with oxidizing agents was not only caused by acid catalysis, but also by the formation of aldehyde groups. Table 9

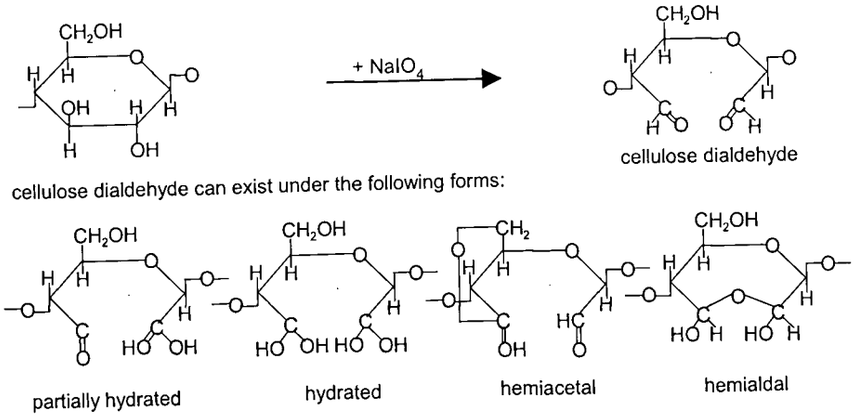

Fig. 7: Cellulose dialdehyde.

gives the data of the 2.5 hour treatment with the two agents. It can be seen that increasing the concentration of the oxidising agent tenfold halved the DP and decreased pH by one unit. This supports the hypothesis that an increased concentration of metaperiodate means an increased number of aldehyde groups in the ring, and the glucosidic bond becomes more sensitive to acid catalysed hydrolysis.

Table 10 and Fig. 6d give the data of Sigma-Aldrich 6288 cellulose. It can be seen that the effects are the same as for Whatman paper. Table 11 compares the DP of the two types of samples after prolonged oxidation (336 h with periodate of different concentrations). Maximum degradation i.e. minimum DP is nearly the same for both kinds of samples and all three concentrations; and also similar to oxidation with NACIO (Table 7).

Infrared spectroscopy

As said above, FTIR analysis, both of untreated paper and of oxidized samples, is complicated because of the high affinity of the samples to water: the peak of the absorbed water is in the region of carbonyl groups and sometimes even covers the C=O band. Also, the identification of the functional groups is complicated because aldehyde, keto and carboxyl groups of oxycellulose absorb in a very narrow region of the spectrum between 1730 and 1780 cm^{-1}. For samples oxidized by metaperiodate the situation is even more complicated because dialdehyde cellulose (Fig. 7) can exist in partially or completely hydrated form, as hemiacetal or as hemialdale, i.e. under forms that do not present a classical peak of the aldehydic carbonyl[10]. It is useful to compare the spectrum of the sample submitted to

Table 12: Presence of the peak at 1720–1740 cm^{-1}.

non-treated samples	treated samples	assignement
no	yes	CHO
yes	yes	CO and CHO*
no	no	COOH**

* The presence of aldehyde groups (CHO) can be deducted by the increase of absorbance after thermic treatment.

** the COOH absorbs at lower frequencies (about 1650 cm-1) and is covered by the band of the absorbed water.

a thermal and vacuum treatment with that of a treatment in the absence of heat. The former showed, at least partially, aldehyde functions under non-hydrated form, visible in the spectrum by a peak around 1750 cm^{-1} that corresponds to the C=O stretching of the carbonyl group (Fig. 8a). In the untreated sample this peak was absent (Fig. 8b).

The results of spectroscopy on the samples oxidized by hypochlorite depended on the pH at which oxidation was carried out. The spectra of the samples oxidized in a slightly alkaline medium (pH = 8) were similar to those of the cellulose dialdehyde. The spectrum of the sample submitted to thermic treatment (Fig. 8c) was different from that of the untreated sample (Fig. 8d), the first showed a peak of the C=O band, the other did not. Oxidation at pH 5 and 12 did not significantly alter the spectra. The only differences were the intensities of absorbancy relative to the OH band and to the absorbed water, which were less intense in the dehydrated, i.e. in the thermally treated samples. In the spectra of the Whatman paper oxidized by hypochlorite at pH 5, the C=O band peak was observed even in the absence of heating (Fig. 8e and 8f). In contrast the spectra of the samples oxidized at pH 12 are characterized by only one value of absorbance in the region of the carbonyl groups (Fig. 8g and 8h). Comparing the spectra of thermally treated and untreated samples is a useful tool to identify certain chemical structures. Table 12 summarizes the differences.

Conclusions

The results of this research support the hypothesis that there is a symbiotic action between acidity and oxidation on the depolymerisation of cellulose. The presence of functional groups formed by oxidation (carboxyl and carbonyl) increases the susceptibility of the β-glucosidic bond to hydrolysis reactions catalysed by a high concentration of hydrogen ions. The nature of the functional groups seems not to

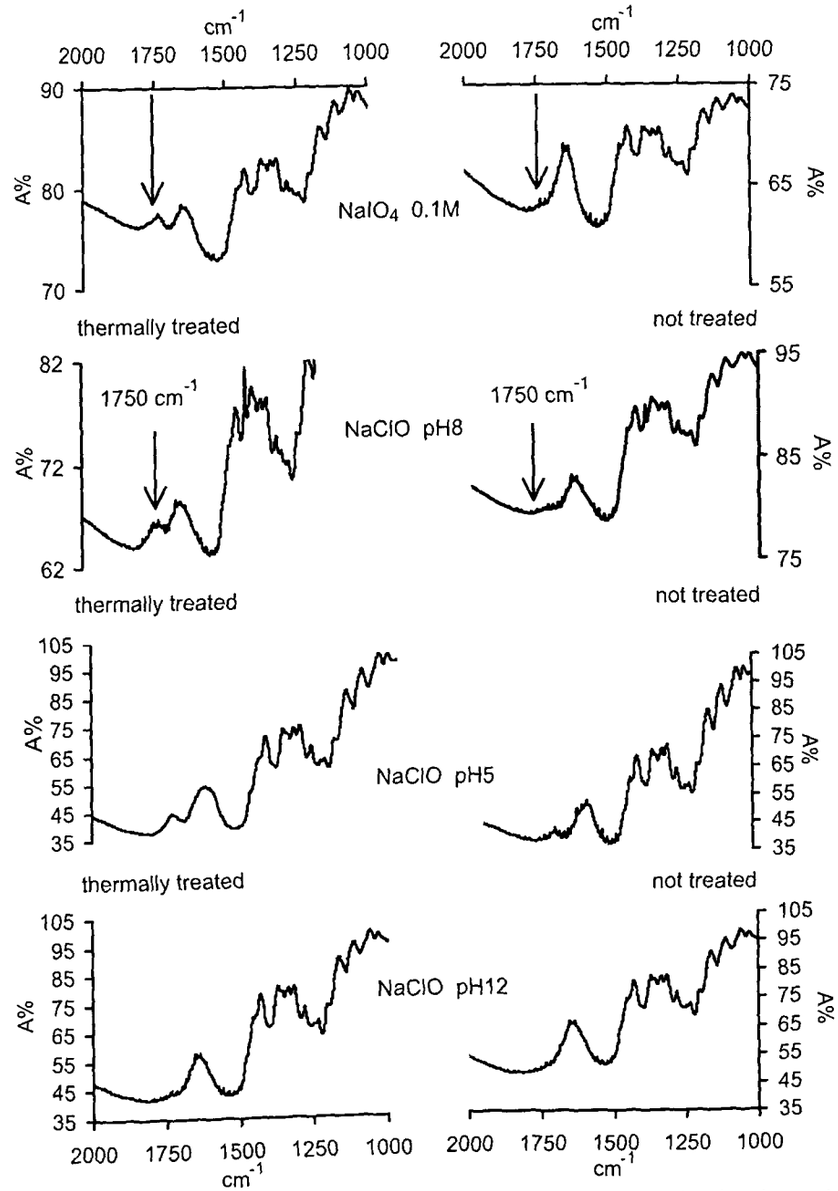

Fig. 8: FTIR spectra of Whatman no. 1 filter paper, thermally treated (left column) or not treated (right column), oxidized for 2 h by: NAIO4 0,1M (first row), NACIO pH8 (second row), NACIO pH5 (third row) and NACIO pH12.(fourth row).

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Papyrus: The Need For Analysis

by FRANÇOISE FLIEDER & ELISABETH DELANGE
IN COLLABORATION WITH ALAIN DUVAL & MARTINE LEROY

INTRODUCTION

Papyrus is one of the oldest writing materials in the world. In ancient times, it was produced from the stem of the reed *Cyperus papyrus* Linné, which was cultivated for nearly 4000 years by the Egyptians on the banks of the Nile. This reed served many purposes: the stem was used as food and in the production of various objects, including carpets, sandals, and boats; the root was employed as a fuel. However, these uses were secondary to the value of *C. papyrus* L. as a writing material. The oldest papyri date from 3100 BC (blank papyrus discovered in the tomb of Hemaka). Papyrus was used in the papal chancellery up to the 12th century AD. This continuity in time has left the curators of museums with an extremely complex collection, in terms of the writings and languages represented. There are hieroglyphic, hieratic, and demotic writings, Greek and Coptic texts, and even Latin, Aramaic and Arabic documents, to which we can add bilingual writings (mainly Greek and Demotic). These major linguistic families witness not only the long course of history, but also the vast selection of subjects covered by this unique material. Thus, the collection of the Louvre, for example, includes a veritable library in which important historical pieces and true works of art with rich illuminations lie next to repetitive sets of documents and simple texts.

THE HISTORY OF A COLLECTION

Papyrus occupies a special place in the history of the collections of the Department of Egyptian Antiquities of the Louvre.

In terms of number it consists of over a thousand Greek papyri but much more Egyptian ones, among them more than a hundred *Books of the Dead*. However, these figures do not correlate to the size of many individual items, as certain Egyptian papyrus rolls are 21 m long, whilst some of the Greek documents are very fragmented.

The papyrus collection was formed in the 19th century. The first were the large collections acquired by the consuls Salt and Drovetti, and later A.P.Ch. Anastasi: 140 by the latter and 103 by the former. Among them were rare pieces, such as the well-known *Papyrus on Astronomy*, fragments of poetry from the Iliad, or the *Mounir Papyrus* dating from Tutmosis III, scrolls of funerary, religious papyri and a large number of legal documents, contracts and letters. The initiators of the collection, who lived at the time when Champollion had just discovered how the Egyptian language worked, already realized that the documents written on papyrus proved to be, not only works of art, but also documents rich in information on the civilization of the Pharaohs. The first entry in Salt's inventory reads as follows, "A long text in a beautiful writing with rubrics and symbolic scenes of great value to the study of Egyptian psychology. The drawing of figures is bold and careful. Perfect preservation." In 1853 the Clot-Bey collection was acquired. It contained pieces of similar value, including the *Neferubenef* and *Hornedjitef* scrolls. The first catalogue of the manuscripts was produced by Théodule Devéria[1] in 1872 and highlighted the wealth of the collection with more than 400 entries, including an almost complete illuminated series of *Books of the Dead*.

In the last quarter of the 19th century, the philologists Paul Pierret and Eugène Révillout made several important acquisitions on behalf of the museum, including a large number of written documents, partly limestone tablets and partly papyri with a mixture of fragments of many different languages. A single entry can include up to some one hundred items (for example, E 6846). As Révillout did not have the opportunity of buying exemplary pieces, he continued, with commendable competence, to extend the demotic collections, which were previously poorly represented in the museum, and to enrich the Greek section. He also acquired homogeneous series, such as the Brugsch collection, consisting mainly of objects from Fayum, or the Chester collection, which was acquired in three stages[2]. These documents are contracts (sales, rents, or marriages). Quite often they are of particular historical value because they include precise dates. However, this specialization in acquisitions was not in accordance with the collection policy of the museum. In 1896 the Museum Council stopped all acquisitions of palaeographic documents and even envisaged their transfer to the *Bibliothèque Nationale*. From then on, the collection was practically frozen. A few acquisitions were made in the 20th century. Some of them were linked to other objects, which was the case with the *Neferubenef Book of the Dead*, others completed a set (for example, the *Nine Magic Papyri* bought in 1995) or filled in gaps, such as the highly decorated papyri from *Sérimen* and *Nespakachouty*. The most spectacular acquisition was that of the *Jumilhac Papyrus* in 1945, which is an important mythological document relating the religious legends of an entire region of Egypt at a relatively late period (Fig. 1).

influence the phenomenon. The results obtained for the paper samples oxidized by sodium metaperiodate ($NaIO_4$), that is for *aldehyde cellulose*, are comparable to those submitted to random oxidation (NaClO).

In order to evaluate and compare the effects of the specific and non-specific oxidation, the samples were submitted to FTIR analysis. The results of the spectrophotometric analysis demonstrated the importance of our sampling procedures for accurate identification of the functional groups introduced by the oxidative procedures in the cellulose molecule. The ability to absorb in the C=O region was influenced by the thermal treatment undertaken prior to analysis. Particularly informative for the identification of the functional groups is the presence or absence of compounds at around 1720–1740 cm^{-1} in the spectrum of the untreated sample.

SUMMARIES

Hydrolytic and Oxidative Degradation of Paper

Two samples of pure cellulose of different degree of polymerisation values were submitted to oxidation degradation by a specific agent (sodium metaperiodate) and by a non-specific agent (sodium hypochlorite). The degradation process was monitored by viscosity measurements in order to check the degree of polymerisation. It is demonstrated that both samples have similar behaviour and that the degradation process results in a common value. The samples were also submitted to FTIR spectroscopy and the results make obvious that different functional groups derive from the oxidation process.

Dégradation hydrolytique et oxidative du papier

Dans cette étude deux échantillons de cellulose pure à différents degrés de polymérisation ont été soumis à une dégradation oxydative par un agent spécifique (sodium métapériodate) et par un agent non-spécifique (sodium hypochlorite). Le processus de dégradation a été contrôlé en effectuant des mesures de la viscosité afin de déterminer le degré de polymérisation. L'étude a démontré que les deux échantillons ont un comportement similaire et que le processus de dégradation aboutit à la même valeur limite du degré de polymérisation. Les échantillons ont été également soumis à une spectroscopie FTIR et les résultats ont mis en évidence que différents groupes fonctionnels proviennent du processus d'oxydation.

Hydrolytischer und oxidativer Abbau von Papier

Es wurden zwei Proben aus reiner Zellulose von verschiedenem Polymerisationsgrad einer Oxidation durch ein spezifisches (Natriumperjodat) und durch ein unspezifisches Mittel (Natriumhypochlorit) unterworfen. An den Proben wurden Viskositätsmessungen zur Bestimmung des Polymerisationsgrades durchgeführt. Es wird gezeigt, daß die beiden Proben ein änliches Verhalten zeigen und daß der Abbau zum gleichen Grenzwert des Polymerisationsgrades führt. Die ebenfalls durchgeführten Messungen mit FTIR-Spektroskopie zeigen, daß sich an den verschieden behandelten Proben verschiedene funktionale Gruppen identifizieren lassen.

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Simona Margutti,
Enrico Pedemonte
Dipartimento di Chimica e Chimica Industriale dell'Università
Via Dodecaneso, 31
16146 Genova, Italy
Tel.: 0039-0103538713
Fax: 0039-0103536199
E-mail: pede@chimica.unige.it

Giuseppina Conio
IMAG-CNR
Via De Marini, 6
16149 Genova, Italy
Tel.: 0039-0106475877
E-mail: conio@imag.ge.cnr.it

Paolo Calvini
Soprintendenza per i Beni Culturali ed Architettonici della Liguria
Via Balbi, 10
16126 Genova, Italy
Tel.: 0039-01027101
E-mail: pacalvin@tin.it

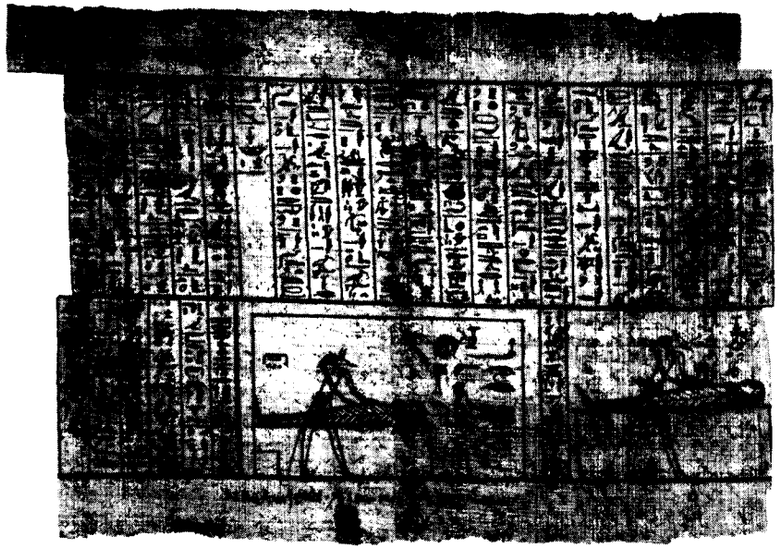


Fig. 1: The Jumilhac Papyrus E 17110 (Ptolemaic period: ca. 140 BC)

It is a special characteristic of the Louvre collection that there was no acquisition of papyri from excavations at the end of the 19th century and, more particularly, in the first half of the 20th century. Apart from the donations of Auguste Mariette, explorer of the Serapeum of Memphis, which included some rare fragments of the Greek poet Alkman, and sacks of fragments from the excavations of Clermont-Ganneau on the island of Elephantine, there have be no real donations from excavations. However, there were some donations given by Egyptologists. They understood the scientific value of the texts they had acquired and were generous enough to offer them to the Louvre. Examples of this kind of acquisition are the *Sarcophagus texts*, donated by Alan Gardiner and Raymond Weill, the *Ramessides Letters* donated by Emile Chassinat, the exceptional *Titular of Rameses II* donated by Stier, and the Gosset donation of the *Pentaour Poem.*

The state of preservation of the collection in the Louvre is extremely variable. The early papyri were stored in rolls, often cut into many smaller sheets and then glued onto cardboard supports for better presentation and documentation. Scattered and fragile fragments were repeatedly moved and re-housed, often without any protection, suffering inevitable damage. Certain pieces have been repeatedly restored, some for the better, others for the worse. Finally, the most spectacular pieces were exhibited for many years in the public galleries of the museum, contrary to modern recommendations on preventative conservation.

LIMITS OF KNOWLEDGE

While the palaeography and the reading of a papyrus document enables the Egyptologist to understand its purpose, most papyri cannot be connected to their archaeological context. Only a few papyri have been accurately dated. We can understand why religious and funerary texts, which were destined to accompany the dead for eternity, remain undated, but this is not the case with administrative documents, where we would expect a precise dating. The oldest samples are also the most rare, for example, the *Abusir Papyrus*, the archives of the Neferirkare temple (Vth dynasty) and the *Mounir Papyrus*, which described deliveries under Pharaoh Tutmosis III. However, some of the most important series of religious papyri cannot be precisely dated.

The condition of the collection has highlighted the need for restoration, which means the need for prior scientific studies. Restoration automatically implies an understanding of the different materials used in the manufacture of the object. Through close contact with the object during its restoration, research can enlighten the methods of its production. This research combines the approaches of a scientist, a curator and a conservator. It aims to understand the techniques and "recipes" used, to follow the working procedures of the craftsman, to analyse the "ageing" processes of the constituent materials and to reveal what might have been the original function of the object. Hence, it touches on disciplines as diverse as cultural history, botany, physics and the many facets of chemistry.

Even though the literature on the production and restoration of papyrus is quite extensive[3–6], many intriguing questions are still unanswered. The following are the most common, which have been posed repeatedly since the first written commentary[7], *Natural History* by Pliny the Elder (1st cent. A.D.), in which he described in detail papyrus production.

- How do the two layers of papyrus stick together? Is it because of alluvium from the Nile[7], sugars liberated by the plant[8,9], the presence of some sort of glue, such as starch[10,11], or the imbrication of the cells provoked by the pressure imposed during the drying process?
- Which part of the stem was used to cut the strips of papyrus[7,12]?
- Why are some papyri whiter than others?
- What is the impact of time on papyrus?

In order to answer these questions, we decided to produce our own papyrus and analyse the various organic compounds and minerals found in ancient specimens. We also examined the behaviour of papyrus in various types of accelerated ageing experiments.

PRODUCTION OF PAPYRUS USED AS A WRITING MATERIAL

The stems of *C. papyrus* L. are triangular in cross-section and can reach 4 m long. First, the stems are stripped, and then the pith is cut into strips[13]. A series of 37- to 45-cm strips, according to the format desired, are laid parallel to each other to make up one layer. A second layer of 10- to 20-cm strips is then laid perpendicularly to the first; this forms the writing surface. The whole is then pressed or beaten, until the sheet of papyrus is completely dry. Scrolls were made by sticking many of these sheets together.

Some researchers have manufactured papyrus[7,14–16] and, using their observations, we made some of our own from the stems of *C. papyrus* L. cultivated in the *Muséum National d'Histoire Naturelle* in Paris. The method described above was used. The papyrus was dried in a press between blotting paper, which was changed regularly. We also tried beating the papyrus in water before the drying procedure. We observed the following.

- The action of the press is sufficient for the adhesion of the two papyrus layers. The addition of glue is therefore unnecessary.
- Strips cut from the lower part of the stem are more translucent and give a better adherence than strips cut from the upper part, which are more opaque.

The colour of the papyrus is related to its thickness. The thinner the papyrus, the quicker it dries, and the whiter the resulting sheet. This can be explained by the fact that *C. papyrus* L. contains enzymes such as phenol oxidase and lactase, which, in the presence of oxygen, acts as a catalysts for the oxidation of the plant phenols. The monophenols are oxidized into orthophenols, which are in turn oxidized into the corresponding quinones; quinones are coloured compounds. This process is the reason papyrus turns brown on contact with air. When the pith of *C. papyrus* L. dries, these enzymes are deactivated and can no longer have any action on the plant phenols. This is why, once the papyrus is finished, the combined action of water and oxygen has practically no effect. This is in accordance with what we have observed in the collections of the Louvre, thicker papyri are darker, whereas the thinner ones are much lighter. A brown discoloration can also be induced by beating prior to drying.

ANALYSIS OF MINERALS

The mineral analysis was carried out by proton-induced X-ray emission (PIXE) using the AGLAE particle accelerator of the *Centre de recherche et de restauration des musées de France* (CRMF).

Description of PIXE analysis with an external beam

The proton beam leaves the accelerator through a kapton window. Because the sample is outside the accelerator, PIXE has the advantage of performing a non-invasive analysis of works of art irrespective of their form or size. At the point of impact of the beam, the object emits X-rays the energy of which is characteristic for the elemental composition of the object. The external beam line of the accelerator comprises a number of different parts[17].

- The document is mounted on a support that can be moved in three dimensions and position the zone of analysis correctly within the particle beam;
- a small camera allows observation of the document and its position from the control room;
- two X-ray detectors are used for low- (<5 keV) and high-energy X-rays;
- a helium atmosphere between the object and the detectors permits the detection of X-rays emitted from the light elements, which would be absorbed by air; all elements above sodium can thus be determined quantitatively.

The detectors are calibrated using thin targets of accurately known elemental composition (in mg/cm^2).

Given the low penetration of 3-MeV protons into solid materials (a few tens of micrometers), PIXE analysis is particularly well suited to the analysis of thin films, such as inks, miniatures, and drawings[18–21].

Experimental conditions

The proton energy is 3 MeV. This is reduced to 2.85 MeV at the sample, after the beam has passed through the 8-mm kapton window. The beam intensity is about 100 to 200 pA. The beam diameter is defined by a tantalum aperture 0.5 mm in diameter. The analyses of the standard samples and the samples themselves are carried out at a constant dose, as measured by the number of particles scattered back by the exit window.

The area of each X-ray line is calculated using the GUPIX program[22]. The apparent concentration in atoms/cm^2 is deduced from calibration curves. This value is then corrected for the self-absorption of X-ray photons by the material; the energy loss of the beam is not corrected.

Results

The most abundant elements detected in all the papyri analysed were sodium, silicon, chlorine, potassium, and calcium (Table 1). Magnesium, aluminium, phos-

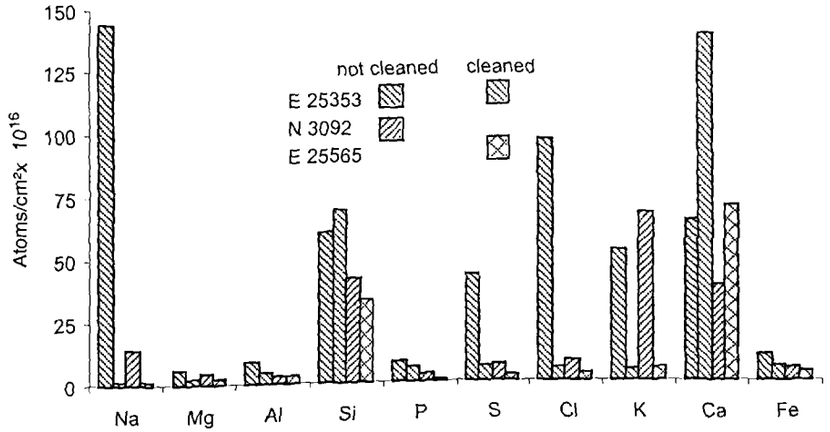
Table 1: Concentrations of elements detected in the papyri using PIXE analysis (atoms/cm^2 x 10^{16}).

	N 3074	N 3092	E 25565 cleaned	E 25353	E 25353 cleaned	N 3265	E 3226	E 3228	E 14703	E 25416
Na	14	14	1.5	144	1.5	90	63	40	55	68
Mg	4.8	4.3	1.6	6.2	2.2	8.8	15	12	9.7	16.7
Al	11	3.3	2.4	9.0	4.5	1.0	12	7.7	9.3	19
Si	48	42	33	60	69	64	41	87	50	98
P	1.8	2.7	0.3	7.8	5.9	7.3	5.5	6.1	4.9	13
S	23	6.7	2.6	43	5.7	14	7.1	6.0	5.6	14
Cl	6.9	8.4	2.9	96	5.2	51	57	6.1	22	107
K	82	67.2	6.0	52	4.7	60	72	84	72	183
Ca	72	38	69	64	138	145	54	66	192	332
Ti	1.4	0.5	0.6	1.3	0.9	1.9	n.d.	2.8	1.5	3.8
Mn	0.3	0.6	0.4	0.5	0..3	0.8	0.3	0.4	0.7	0.8
Fe	1.0	5.3	3.9	10	6.2	1.3	6.9	3.4	6.9	14
As	0.9	3.5	2.3	n.d.	n.d.	n.d.	n.d.	8.3	n.d.	n.d.
Br	0.1	0.1	0.1	0.2	0.1	0.1	0.3	n.d.	0.1	0.3
Sr	0.2	0.1	0.2	0.2	0.1	0.2	0.1	0.1	0.1	1.0
all	**267**	**197**	**127**	**494**	**244**	**445**	**334**	**330**	**430**	**706**

phorus, and iron were usually present, but in lower concentrations. Traces of titanium, manganese, bromine, and strontium were present. Arsenic was found in only a few fragments.

In the case of the papyri that had not been cleaned, most of the elements detected came from the surface layer of pollution. This is particularly the case with the low-energy X-rays, which correspond to the lighter elements. For the high-energy X-rays, the corresponding elements may come from the surface layer or the papyrus itself, provided the energy is high enough for the X-ray photons to cross the layer of pollution without being absorbed too much. A previous study has shown that total mineral content of modern papyri is no higher than 100 x 10^{16} atoms/cm^2. Table 1 shows that the papyri analysed had a variable degree of pollution by various polluting agents. In the papyri that had not been cleaned, the mineral content varied from about 200 x 10^{16} atoms/cm^2, for the least polluted papyrus (N 3092), to more than 700 x 10^{16} atoms/cm^2 for the most polluted sample (E 25416).

The main polluting agent for all the papyri that have not been cleaned (except N 3074 and N 3092) appeared to be salt, characterized by sodium, chlorine, and traces of bromine. This contamination is characteristic of many Egyptian objects. Potassium, which is present on all the papyri, could be associated with the salt.



Fig, 2: Histograms of mineral element content demonstrating the effect of washing.

However, the two papyri that contain very low amounts of sodium (N 3074 and N 3092) both have high potassium contents.

The second polluting agent is calcium, which seems to exist on the papyri as its carbonate. However, the presence of small amounts of sulphate and phosphate cannot be excluded.

The third polluting agent is silicon, which is present on all the samples probably in the form of a mixture of quartz and earth and which can be characterized by aluminium, iron and manganese, among others.

Traces of arsenic were found on four papyri (N 3074, E 3228, and two fragments of the same papyrus, N 3092 and E 25565). These documents were probably contaminated with arsenic pigments (orpiment) either during being inscribed or by contact with the environment in which they were found.

Effect of cleaning upon polluting agents

As there were two pairs of fragments from the same object, one of them cleaned and the other not cleaned (two fragments of papyrus E 25353 and N 3092, which remained dirty and E 25565, which was cleaned), it was possible to determine the effect of washing with water. The elements mostly affected by cleaning are those which form water-soluble compounds (Fig. 2), i.e. sodium, chlorine, potassium, and sulphur. The rare earth elements, aluminium and iron are removed by washing. Silicon is relatively stable. The amount was increased during washing in one case and decreased in another. Calcium increased in both cases, probably

due to the temporary hardness of the washing water. However, another and possibly more feasible hypothesis is that when the pollution layer is removed by washing, only the elements in the papyrus itself are analysed. The same may apply for silicon. This effect is less obvious for the other elements because it depends on the difference between the concentration in the pollution layer and that in the papyrus itself.

Special case of the Abousir Papyrus (E 25416)

One of the fragments analysed in Table 1 (E25416) shows exceptionally high calcium and also a quite high sulfur content levels. X-ray diffraction analysis of the surface of a sample revealed the presence of calcium sulphate in the form of gypsum. Also zinc (not reported in Table 1) is to be found in this fragment, but the relevant compound was not identified. Electron microscopy of that sample confirmed the presence of sulphur and calcium, and showed that the zinc was localized in submicron grains attached to the calcium sulphate. The presence of these two compounds in these fragments remains unexplained.

ANALYSIS OF ORGANIC ELEMENTS

Starch

C. papyrus L. contains native starch, which is situated around the conducting fiber. The form in which starch is found in papyrus used as a writing support is an important key to know how papyrus was manufactured in the past.

Our method was to cut sections using a freezing microtome, stain them with lugol for study under the optical microscope[23, 24]. We analysed two types of ancient papyrus.

- Undated papyri of uncertain origin, provided by the department of Egyptian Antiquities in the Louvre.
- Papyri dating from between the 3rd century BC and the 8th century AD, which mostly came from papyrys cardboard (i.e. several sheets stuck together); given by the Sorbonne Institute of Papyrology.

Altogether, fifteen papyri were thus examined under the optical microscope, and classified into three categories.

- Starch was totally absent in three of the samples from the Sorbonne Institute of Papyrology (Sorb. 1, Sorb. 3, and Sorb. 6). The various restoration treatments to which these objects had been submitted could explain this observation.

Fig. 3: Section of papyrus Copte 1. Left: A longitudinal section of the conducting fibers with the burst starch grains on the surface. Right: Transversal section of another fiber. The endogenous starch appears darker and can be seen as grains inside the papyrus and as starch on the surface (x 190).

- Seven papyri only contained endogenous starch (A2, A6, A7, Copte 1, Sorb. 2, Sorb. 4, and Sorb. 7). These samples must, therefore, have been manufactured without the addition of a starchy glue.
- The density of the starch grains varies greatly among the papyri. This can be explained by the age of the *C. papyrus L.* stem when it was harvested and dried by exposure to the sun. Two of the papyri were found to have grains of starch that had burst due to thermal effects experienced over the centuries (Fig. 3).
- A starchy glue was found on five of the papyri (A3, A4, Copte 2, Copte 3, and Sorb. 4). Two of these (A4 and Copte 2) were made of three layers (Fig.4), between which glue was found. In these cases, the starchy glue was found in the join of two sheets of papyrus from the same scroll. Wheat and barley flours were identified in the glues. Indeed, the size of the intact grains looks very much like these cereals. In two other samples (Copte 3 and Sorb. 4), a starchy paste was found on the surface of the papyrus. They came from the Sorbonne Institute of Papyrology and were found as *papyrus cardboard*, made from many layers of papyrus stuck together.

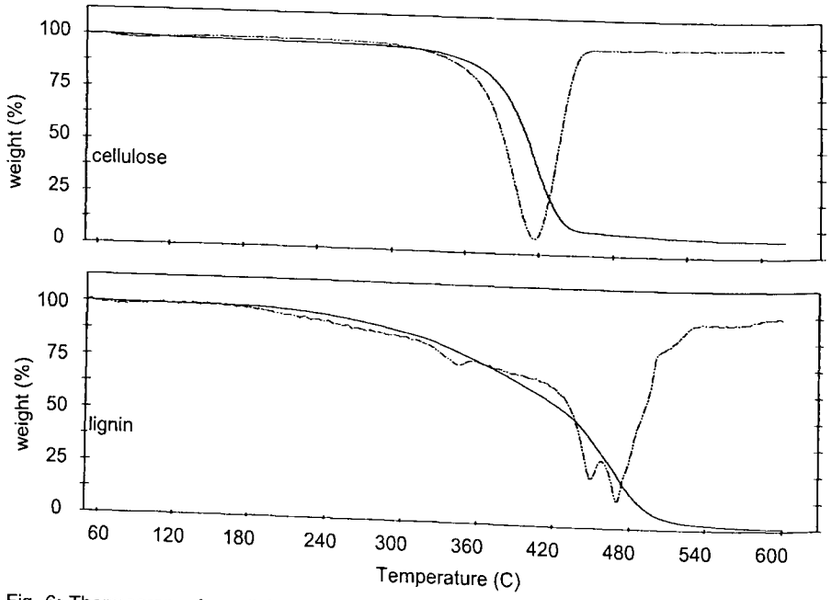


Fig. 6: Thermograms for cellulose and lignin. The broken line is the "First Derivation" of the thermogravimetric curve.

height of the peaks in the derivative curve. We can also see the relative quantities of the various components, by calculating the area of each peak. In order to identify the precise nature of each peak, we did the same thermogravimetric experiment with pure cellulose and lignin (Fig. 6).

Results

Because of the large amounts of mineral compounds detected on the ancient papyri, the relative concentrations of organic compounds was calculated following deduction of the percentages of ashes and water linked to each sample (Table 2). Fig. 7 gives the thermograms of modern white, modern brown, the *Abousir Papyrus* (Louvre E 25416) and the papyrus Sorbonne 3. The following can be observed.

- The thermal degradation of papyrus is divided into three stages corresponding to the loss of the following products:
  - between 100 and 250°C: bound water
  - between 250 and 380°C: cellulose
  - between 380 and 600°C: lignin

Table 2: Relative values (percent)of cellulose and lignin (after deduction of bound water and ash) in modern and ancient papyri.

	modern white	modern brown	E 25416	S3	S4	S5	S6	S7
cellulose (and decomposition products of lignin)	60	68	58	67	66	61	60	58
lignin	40	32	42	33	34	39	40	42

- When the pure products are analysed decomposition occurs in a narrow temperature range and the peak in the derivative curve is very sharp. Cellulose provides a striking example of this (Fig. 6).
- The percentages of cellulose and lignin found in the modern papyri (Table 2) are in agreement with the results found by others[25]. The brown, highly oxidized papyrus has a different thermogram from the white papyrus. During the ageing of papyrus, lignin degrades first. The decomposition products of lignin become volatile in the same temperature range as cellulose (Fig 8: brown pap.). The peak due to cellulose is thus broader, and that due to lignin narrower.
- It would be premature to draw, on the base of the results found in this research, any conclusions for the ancient papyri. Nevertheless, we can hypothesize. The papyri E 25416, Sorb. 5, 6 and 7 have percentages of cellulose and lignin similar to the modern white papyrus and appear to have undergone little oxidation. However, Sorb. 3 (Fig. 7) appears to be more degraded and the very low concentration of lignin in Sorb. 4, in which the pollution layer seems to have been cleaned with acid (recognizable by the low concentration of ash), reflects a strong deterioration.

These preliminary results are very promising, but should be interpreted with caution, considering that the initial cellulose-lignin ratio can vary from one papyrus to another depending on a number of parameters such as the season of harvest, geographic origin, the technique of manufacture and the current state of the manuscript.

In order to provide information to help date ancient papyri or determine their place of origin, we are planning to study the relative concentrations of cellulose and lignin in fresh papyrus stems grown in different regions (France, Egypt, and Sicily) and harvested in either spring or autumn. We will also analyse different parts of the stem. It is also important to extend our collection of samples and study many more papyri of known date and location.

Fig. 4: Section of papyrus A4. Three layers are visible. A starchy paste (darker area) has been used between the two layers (x 190).

Finally, we analysed a join from a Greek papyrus (A3), in which a starchy glue was also used. Some of the very small starch grains remained intact (2 mm x 4 mm in size) but these cannot be attributed to any known starch (Fig. 5).

Thus, it became obvious that no glue was used to stick together two papyrus layers during manufacture. Starchy glue seems to have been used only to stick two sheets of papyrus to make a scroll or to make *cardboard* at a later date.

Cellulose and lignin

Papyrus is mainly composed of holocellulose, comprising cellulose (54–60%) and hemicellulose, and of lignin (36–40%)[13] their proportions determined by location and season.[24] These polymers are organized according to different morphologies (α-, β-, and γ-cellulose).

The problem is to find out whether the relative proportions of these components can be used to characterize a papyrus and determine its state of preservation. To examine this hypothesis we have analysed by thermogravimetry papyri from different epochs and various geographic locations[25]

Thermogravimetry analysis is a simple, rapid and reliable method requiring a small sample. It involves monitoring the loss in mass of a material as a function

Fig. 5: Section of papyrus A3. Left: the black vertical band corresponds to a starchy glue. Intact grains can be observed near the center of photo (x 470).

of temperature (dynamic analysis) or as a function of time at a given temperature (isothermal analysis). The change in mass corresponds to a range of physical and chemical processes, which can be used to characterize the various components by studying their degradation curves. In the case of a composite material, such as papyrus, dynamic analysis has proved to be the most useful.

Experimental conditions

These experiments were carried out using a TGA7 Perkin-Elmer thermobalance, which operates in the 50 to 600°C temperature range with a heating grate of 10°C per minute. The purge gas is a mixture of oxygen (20%) and nitrogen (80%) and is injected at a pressure of 1.35 bar[26]. The sample weighs about 1 mg.

We worked on samples of dated papyri (Sorb. 5, Sorb. 6, Sorb. 7 and *Abousir Papyrus* E 25416). Two modern papyri manufactured in Egypt were also analysed. One was very light; it was made in a press. The other, which was brown, was beaten before being dried.

In the thermograms presented below, we can see the rate of degradation of cellulose and lignin, which is characterized by the slope of the curves or the

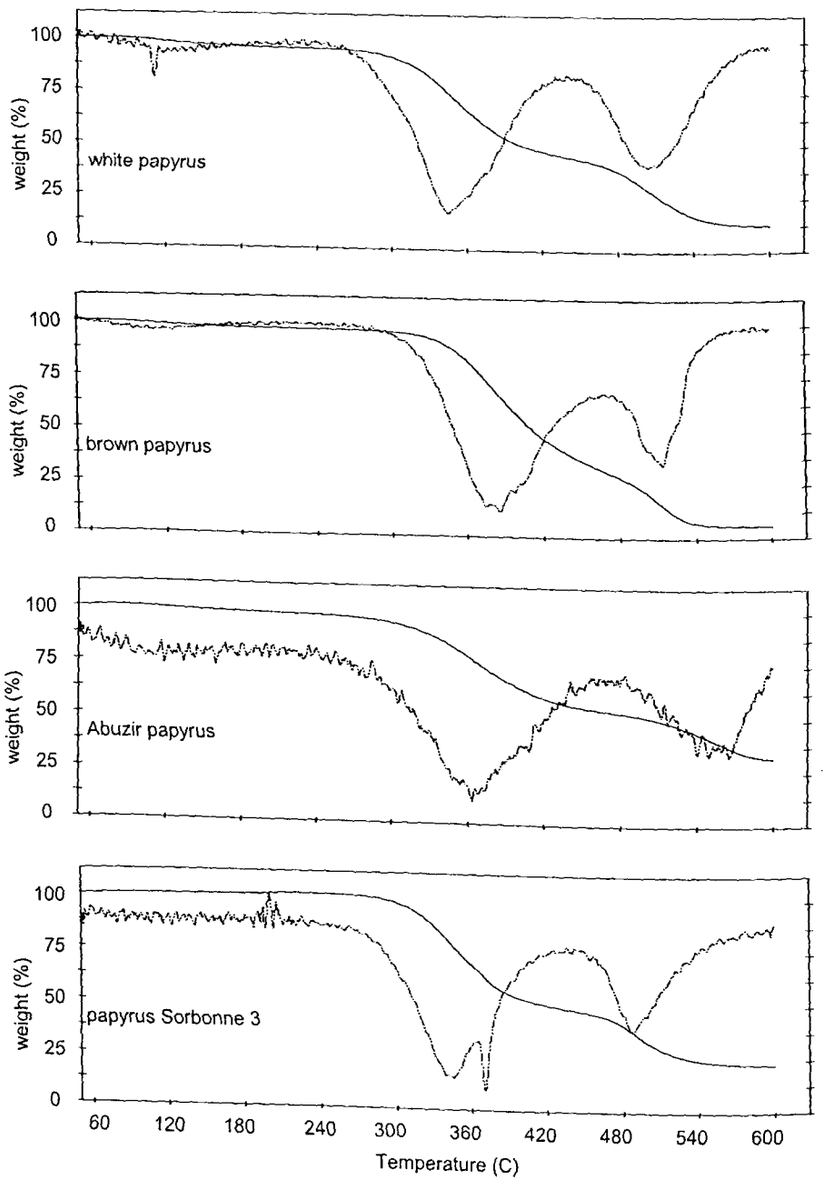


Fig. 7: Thermograms for the modern and antique papyri. The broken line is the "First Derivation" of the thermogravimetric curve.

Table 3: pH of the modern papyri after accelerated ageing by moist heat (80°C 65% RH), light (25°C 50% RH) and pollution (SO_2 + NO_2).

	80%65%		Light		Polluted	
	white	brown	white	brown	white	Brown
control	7,7	6,8	7,7	6,8	7,7	6,8
1 week	7,0	6,5	7,2	5,3	6,1	
2 weeks	7,1	6,3	7,0	5,0	5,1	3,3
3 weeks	6,9	5,8	7,0	4,7	4,7	
6 weeks	6,3	5,7	6,9	4,4	3,9	1,9

STUDY OF THE DEGRADATION OF PAPYRUS

To define the best conservation conditions for ancient papyri, we decided to study the behaviour of papyrus in the presence of the principal agents causing physical and chemical degradation: heat, humidity, light, and pollution. We have thus analysed the behaviour of two modern papyri (white and brown) in the presence of these various aggressive agents.

Experimental conditions: Choice of ageing and tests

In order to monitor the kinetics of the degradation, the papyri were analysed after 2, 3, and 6 weeks exposure to three types of aging:

- Heat and humidity according to the IPSO 5630/3: 80°C, 65% RH.
- Light irradiation: 1500-W xenon lamp at 25°C, 50% RH.
- Pollution in an atmosphere containing 20 ppm NO_2 and 10 ppm SO_2 at 30°C, 50% RH.

For describing the degradation of the aged papyri we measured the mechanical strength (zero span tensile strength), acidification (pH), optical constant (whiteness) and oxidation (copper number).

Results

The results of pH measuring are presented in Table 3, those of whiteness and oxidation in Fig. 8. The following general conclusions can be drawn:

- Tensile strength: Because of the heterogeneity of the fibres in papyrus, the results obtained from the zero-span measurements are too dispersed to allow a reliable interpretation.

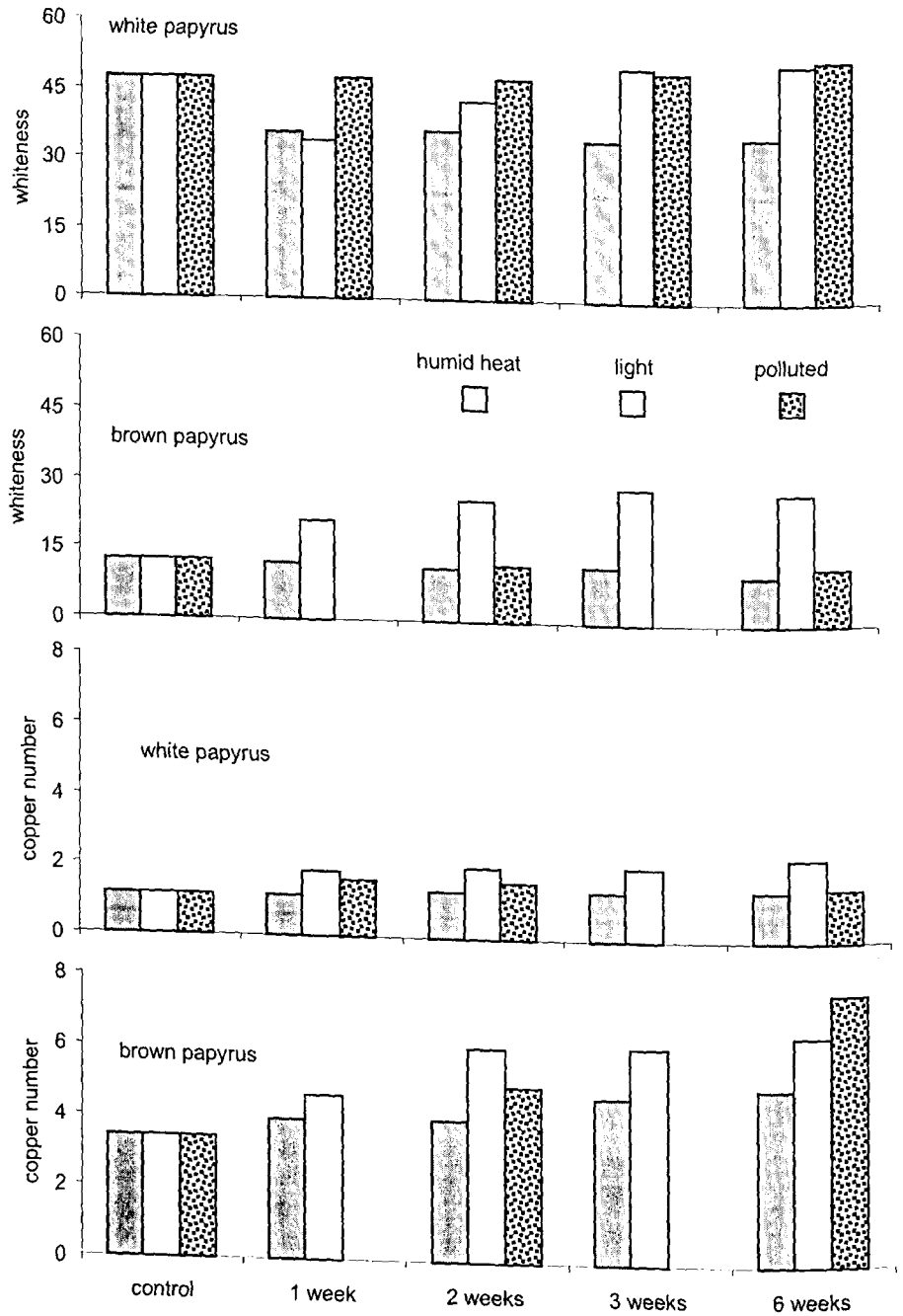


Fig. 8: Variations in the degree of whiteness and copper number of the modern white and brown papyrus.

- pH: After 6 weeks, pollution causes a significant acidification of the white papyrus, and a pronounced drop in pH for the brown papyrus. We noted that brown papyrus was also acidified after accelerated ageing with light (Table 3).
- Whiteness: Only the white papyrus yellowed under the action of heat. This appeared in the first week and then stabilized. The behaviour of the papyri upon exposure to light was very different. After 1 week's accelerated ageing, the white papyrus had yellowed, but then, with ongoing exposure to light, became progressively whiter. The brown papyrus rapidly became lighter from the beginning. (Fig. 8).
- Oxidation: The main observation was that the copper number of the non-aged brown papyrus was three times higher than that of the non-aged white papyrus. This indicated that the beating of the pith had led to a significant amount of oxidation in the material. Following accelerated ageing due to light, both papyri suffered significant oxidation. The oxidation of the brown papyrus, after 6 weeks exposure to pollution and to light, reached values too high to be measured (Fig. 8).

These results show that, during accelerated ageing, the white papyrus reacts much better than the brown papyrus. This can be explained by the high degree of oxidation of the brown papyrus, due to its method of manufacture.

The acidification caused by six weeks exposure to pollution appears to have little effect on the cellulose in the white papyrus, but has more effect on the brown. Light causes negligible degradation of both types.

CONCLUSION

This study has shed new light of the technique of manufacture of papyrus as a writing material. We can draw several conclusions.

- No glue was added for the adherence of the strips.
- The sheets made with the lower part of the plant are more translucent and stick together better than sheets made from the upper part of the plant.
- The sheets dried after beating are very brown and contain highly oxidized cellulose.

The analysis of the mineral and organic elements in the ancient and modern papyri provided an opportunity to test a number of different analytical methods. Considering the valuable nature of the documents concerned, we have obviously favoured non-destructive methods, or those which required very small samples. Some proved to be more appropriate for our studies, while others remain very promising.

We have, thanks to the PIXE method, analysed the mineral content of the papyri. The identification of the chemical content in the pollution layer of each papyri reveals the influence of the cleaning process. However, the analytical results are difficult to interpret because the mineral content of the papyrus itself can interfere and also the elementary analysis gives little information on the chemical compounds present in the pollution layer.

Regarding the organic compounds, we used thermogravimetric analysis to measure the respective concentrations of cellulose and lignin in some modern and ancient papyri. The results brought us to form the hypothesis that there is a correlation between the cellulose-lignin ratio and the condition of papyrus.

Our experiments will be continued and be extended, not only in order to confirm this hypothesis, but also in order to find a better understanding of the history of papyrus conservation, alterations and any treatment that such an object may need at present. We hope that this technique may also prove to be useful in dating and locating the origin of papyri.

This work has also brought a result for practical conservation. The behaviour of modern papyri during accelerated ageing has demonstrated the disastrous consequences of exposure to light. This very important point should be taken into account for exhibiting papyrus collections.

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We would like to express our thanks to Prof. Blanchard, who kindly provided the ancient papyri. We thank M.C. de Bignicourt, who has done the analysis regarding starch, Prof. Roland, Michel Abadie and Monique Mousiniak, who helped with them and Prof. Vairon for his help in the interpretation of the thermograms. We also thank the team at the AGLAE accelerator of the C2RMF for their help during the PIXE analyses.

SUMMARIES

P*apyrus: The Need For Analysis*

Papyrus, one of the most ancient supports for writing, is made from the heart of the reed *Cyperus Papyrus L.* As the Egyptian Antiquities Department of the *Musée du Louvre* has a famous and significant collection of papyri, it is of great importance to understand the mechanics of this material and monitor the condition of these manuscripts. Historians still have many questions concerning the manufacturing techniques of papyrus and so an attempt was made to answer a few of them by examining some dated and undated fragments from the Louvre and the *Institut de Papyrologie.* Analysis of the mineral and organic elements, in particular starch, showed that the plant material strips, which make up a papyrus, adhere to each other without any additional glue.

The researchers also tried to predict experimentally how these documents would deteriorate over time, by submitting some modern papyri to artificial ageing cycles. Light proved to be the most deteriorating factor, a very important parameter, which must be taken into account when exhibiting the collections.

Papyrus: La nécessité d'analyse

Les papyrus, qui constituent l'un des plus anciens supports de l'écriture, sont fabriqués à partir de la moelle d'un roseau, le *Cyperus Papyrus L.* Le département des Antiquités Egyptiennes du Musée du Louvre ayant une importante et très prestigieuse collection de papyrus, il était intéressant d'analyser et de étudier l'état de conservation de ces manuscrits. Leurs techniques de fabrication faisant encore l'objet de nombreux questions de la part des historiens on a essayé de répondre à certaines d'entre elles en étudiant quelques fragments, datés ou non, provenant du Musée du Louvre et de l'Institut de Papyrologie . L'analyse des éléments minéraux et organiques, en particulier l'amidon, a permis d'observer que les bandes adhéraient entre elles sans qu'aucun ajout de colle.

Par ailleurs, le comportement dans le temps de ces documents a été suivi en soumettant des feuilles de papyrus modernes à des cycöes de vieillissement artificiel. La lumiére s'est avérées l'agent de détérioration le plus agressif. Ce paramètre très important doit être pris en compte lors des expositions des collections.

Paprus: Der Bedarf an Analyse

Papyrus, einer der ältesten Beschreibstoffe, ist hergestellt aus dem Mark der Schilfpflanze *Cyperus Papyrus L.* Die Abteilung für Ägyptische Antiquitäten des Louvre-Museums besitzt einen bedeutenden und berühmten Bestand, und eine Untersuchung des Erhaltungszustandes derselben sowie der Herstellungsweise von Papyrus erscheint angebracht. Über letzteres sind sich Historiker immer noch nicht voll im Klaren. Deshalb wurde versucht, einige davon aufgrund der Analyse einiger datierter und undatierter Fragmente aus dem Louvre und dem Institut für Papyrologie zu beantworten. Die Analyse der mineralischen und einiger organischer Bestandteile, insbesondere Stärke, ergab, daß das pflanzliche Material, aus dem Papyrus besteht, ohne Zugabe eines Klebemittels aneinander haften.

Die Untersuchung galt auch der langfristigen Dauerhaftigkeit. Einige moderne Papyri wurden einer beschleunigten Alterung unterworfen. Licht erwies sich als der am meisten schädigende Faktor: eine wichtige Erkenntnis, die bei der Ausstellung von Papyrus-Objekten bedacht werden muß.

APPENDIX: LIST OF PAPYRI ANALYZED

Non-dated papyri

Papyri from the Department of Egyptian Antiquities of the Louvre:

- A1, A2, A3, A4, A5, A6, A7, Copte 1, Copte 2, Copte 3, Grec 1, Arabe 1. These papyri come from very diverse batches of papyri, principally from the

excavations either on the island of Elephantine or Sakkara; they are practically intact since their discovery.

Dated papyri

Papyri from the Department of Egyptian Antiquities of the Louvre

- **E 25416.** *Abousir Papyrus.* Old Kingdom (2780–2190 BC). This was found in the funerary temple of the King Neferirkare and constitutes the archives of the temple for the epoch 2390–2250 BC. (Two fragments analysed with 5-point PIXE analysis).
- **E 14703.** Fragments of sarcophagus texts dating from the Middle Kingdom (2160–1780 BC), which show the unusual fashion in which the funerary texts were inscribed on coffins. (One fragment analysed with 4-point PIXE analysis).
- **E 3226.** Epoch: 1478–1426 BC (New Kingdom). This papyrus is an accounting document for the years 28 to 35 of the reign of King Tutmosis III (18th dynasty) from Thebes, where it was acquired by the collector Anastasi. (One fragment analysed with 3-point PIXE analysis).
- **N 3092.** Book of the dead, 18th dynasty. (Five fragments analysed with 8-point PIXE analysis).
- **E 25565.** Book of the dead, 18th dynasty, same papyrus as N 3092. (Two fragments, cleaned, and analysed with 6-point PIXE analysis).
- **N 3074.** Book of the dead, 18th dynasty. (Two fragments analysed with 6-point PIXE analysis).
- **E 25353.** Literary and count texts, 3rd intermediary period. (Two fragments, cleaned and not cleaned, analysed with 9-point PIXE analysis).
- **E 3228.** Epoch: 690–664 BC, same collection as papyrus E 3226, describes a special justice ruling in year 6 of King Taharqa, 25th dynasty. (One fragment analysed with 4-point PIXE analysis).
- **N 3265.** 103–102 BC under Ptolemy X, describing an act of donation. (One fragment analysed with 5-point PIXE analysis).

Papyrus from the Sorbonne Institute of Papyrology:

- **Sorb. 1.** Ptolemic period, 3rd century BC. This papyrus has been restored using an enzymatic method.
- **Sorb. 2.** Roman period, 2nd century AD.
- **Sorb. 3.** Byzantine period, 8th century AD.

- **Sorb. 4.** Ghoran period, 3rd century BC. This papyrus has been restored with hydrochloric acid.
- **Sorb. 5. Reinach** 19. Date: 108 BC.
- **Sorb. 6.** Reinach 94. Date: AD 193–98.
- **Sorb. 7.** Reinach 105. Date: AD 432.

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included in the trials the Whatman Paper, in order to check, once again, the effects of irradiation on those chemical and physical properties that can be measured only on pure cellulose, for example the degree of polymerisation.

The main negative effects of radiation on the paper (observed through viscometric and infrared spectroscopic measurements) are: the formation of unsaturated components, which do not pertain to the structure of the polymer, and the depolymerisation of cellulose, which is proportional to the absorbed radiation[4]. The ageing of paper also influences these effects. Therefore, it was decided to combine the radiation treatment with other treatments that could moderate the formation and the action of free radicals, which are principally responsible for the depolymerisation of cellulose[5]. Two series of experiments were arranged: the effects of oxygen removal in the first, and water soaking in the second. This latter experiment also attempted to simulate the effects of irradiation on already deteriorated paper, imitating, for example the situation after a flood. Moreover, we controlled the *in vivo* effect of radiation on the microbial flora. Finally, the effect of irradiation after a certain time was verified. All the samples, having undergone the different experimental treatments, were compared with a similar series of samples. which were submitted to accelerated ageing.

In brief, the objectives of the present work were:

- to verify the effects of radiation on commercial paper and, for some parameters, on cellulose;
- to confirm the effect of the ionising radiation to reduce the microbial flora;
- to verify the ability of some treatments associated with irradiation: to increase the decontaminating action of radiation, and/or to reduce the negative effects of irradiation on paper;
- to verify the action of irradiation on paper over time.

The objective of the experimental work was not only to find the most relevant structural changes induced by the decontamination treatment. We also aimed at evaluating the effects of these changes, in view of a costs/benefits analysis, which has to be calculated before proposing the method on a large scale.

MATERIALS AND METHODS

Cellulose and paper

A commercial paper, manufactured by the Cartiere Miliani SpA, was selected for the trials. This paper is a "permanent paper", one that is able, in principle, to stand a long ageing period of several hundred years without suffering substantial

changes and one that complies with ISO 9706. Fibre: 100% chemical pulp (ca. 40% softwood). Filler: calcium carbonate. Sizing: cationic starch and alkyl-diketene. Additional surface sizing: a mixture of natural and synthetic substances, such as oxidized cornstarch and an acrylic compound. Other additives: a fluorescent whitening agents, small quantities of blueing agents and sodium chloride.

Whatman Paper n.1 (Carlo Erba SpA) was used to determine the effects of radiation on cellulose.

Irradiation technologies

Paper irradiation was performed at the *Calliope* plant of ENEA in its Research Centre at the Casaccia (Rome, Italy). The Calliope plant is a pool-type irradiation facility equipped with a Co-60 source, having a cylindrical geometry, with maximum nominal activity of 3.7×10^{15} Bq.

To determine the levels of the pre-set doses that had to be applied in this experimental programme, we used the Fricke dosimetry according to the ASTM Standard D 1671-72: *Absorbed gamma radiation dose in the Fricke dosimeter.* Doses of 2 and 5 kGy were administered using a dose/rate of 14.700 Gy h^{-1}, where the Gray (Gy) corresponds to an absorption of ionising energy equal to 1 Joule per kg of treated material. For the microbiological trials, also the dose of 3 kGy was tested. Such dose/rate was chosen because, in previous irradiation experiences on Whatman Paper (where the dose/rates were 323 Gy h^{-1} and 16.400 Gy h^{-1}), we observed that more unsaturated compounds developed and a larger degradation of cellulose occurred, at the lower dose/rate for equal amount of absorbed dose. In that experience, the degree of polymerisation (DP) and the infrared spectra (IR) were utilised. In fact, the formation of carbonylic compounds (more than 15% of CO mmol) and structural changes could be observed only when a lower dose/rate and an irradiation dose greater than 10 kGy were applied.

Associated treatments

Before all treatments, the samples were conditioned at 23°C and 50% RH according to ISO 187. Four groups of samples were prepared:

- Z: No pre-treatment.
- V ("Vacuum"): Put into plastic bags (PE - PP), deprived of atmospheric oxygen through air aspiration (99.9 % vacuum) by the MiniPack MV50 apparatus).
- N ("Nitrogen"): Same as V, but, prior to sealing, the samples were washed twice with nitrogen.

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Françoise Flieder
Directeur de Recherche émérite du C.N.R.S.
Centre de Recherche sur la Conservation des Documents Graphiques
36, rue Geoffroy St.Hilaire
75005 Paris
France
E-mail: fflieder@club-internet.fr

Elisabeth Delange
Conservateur en chef au Département des Antiquités Égyptiennes
Musée du Louvre
75058 Paris Cedex 1
France

Alain Duval
Ingénieur
Centre de Recherche et de Restauration des Musées de France
75041 Paris Cedex 01
France
E-mail:alain.duval@culture.gouv.fr

Martine Leroy
Asistant Ingenieur
Centre de Recherche sur la Conservation des Documents Graphiques
36 rue Geoffroy St. Hilaire
75005 Paris
France

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Gamma Radiation Treatment of Paper in Different Environmental Conditions

Chemical, Physical and Microbiological Analysis

by M. ADAMO, M. BRIZZI, G. MAGAUDDA, G. MARTINELLI, M. PLOSSI-ZAPPALÀ, F. ROCCHETTI & F. SAVAGNONE

INTRODUCTION

This study is part of larger research, which aims at finding new systems for the decontamination of books and documents, stored in libraries and archives, which are damaged by biological organisms such as insects and mildews.

At present, decontamination is usually performed with treatments based on ethylene oxide, a harmful product utilisation of which will no longer be allowed in the future for such purposes. Therefore, alternative methods, such as ionising radiation and particularly gamma rays, are presently being investigated and evaluated.. These, if compared with other types of radiation, have the advantage of a higher penetrating power. Therefore, we can treat considerable amounts of damaged material. In addition, irradiation with gamma rays does not cause subsequent problems and leaves a restored material free from contaminants.

Previous experiences[1] showed the reducing effect of the ionising radiation on the microbial flora and, at even lower doses, on insects[2]. In another work[3], the reaction of Whatman Paper n.1 to gamma radiation was examined. Whatman Paper n. 1 was chosen as a reference material, because it is made of pure cellulose without fillers or sizing. Therefore, it is possible to measure the effects of any treatment on the main component of paper, without interference from other elements.

In the present study, a permanent, commercial paper, manufactured with chemical pulp was examined. This paper does not contain lignin and is suitable for the conservation of documents. The study was performed by testing the chemical, physical and mechanical properties of the paper before and after radiation treatment. The treatment was set with the same dosage of gamma rays thought to be necessary for a future standard treatment of decontamination. We

- S ("Saturated"): The samples were put in plastic bags and saturated with tap water.

V and N were done in order to study the influence of oxygen, S in order to study the influence of water. After treatment all bags were automatically sealed by the same apparatus MiniPack MV50 and then exposed to irradiation.

To verify the effects of radiation after time, accelerated ageing was performed according to ISO 5630/3 80°C 65% RH, but for 12 days.

Measurement of physical and chemical properties of commercial paper

All samples were characterised by measuring the following chemical and physical properties:

- Mechanical properties, measured in the machine direction (MD) and in the cross direction (CD)
  - tensile strength (ISO 1924-2)
  - tearing resistance (ISO 1974)
  - folding endurance (ISO 5626)
  - stretch at break (ISO 1924-2)
- Optical properties
  - diffuse blue reflectance factor (ISO brightness) (ISO 2470)
  - light absorption coefficient using Kubelka-Munk Theory (ISO 9416)
  - light scattering coefficient using Kubelka-Munk Theory (ISO 9416)
- Colour measurements. The colour measurements were performed with the spectrophotometer Perkin-Elmer Lambda 15, using an integrating sphere. The space colour CIE L*a*b*, the Illuminant D_{65}, the 10° observer angle and the measuring geometry d/8°, were adopted.
- Chemical properties
  - Hydrogen ion concentration (pH) of the paper extracts (ISO 6588; cold extraction)
  - Kappa Number (degree of oxidability) (ISO 302)
- FTIR measurements. For FTIR (Fourier Transform Infrared) spectrophotometric analysis, a Nexus-Nicolet instrument was used, dispersing the samples in KBr pellets. Spectra were obtained by transmission in the range 5000–350 cm^{-1}, in resolution 2 (0.964 cm^{-1}), mediating on 128 scans. The spectra obtained in this way were re-read as they were, or normalised at suitable

frequencies either as a second derivative or through procedures of curve fitting and doing a deconvolution according to Fourier.

Results of physical and chemical property measurements (average of 10 measurements; only 5 for the colour measurements) are given in Tables 1–8. Transmission FTIR spectra are given in Figs. 1–2.

Statistical analysis

An analysis of variance and Tukey's test[6] for the mean separation were done for each measured variable. Tukey's test is normally set up to test if pairs of means are different. The letters displayed in Table 1–7 Column T symbolically indicate the results of Tukey's test: means are not significantly different at α level 0.05 if they have at least one letter in common.

For each paper property, the statistical analysis aimed at answering the following questions:

- Does irradiation affect the paper properties? At what dose? What if the dose is increased from 2 to 5 kGy?
- If the paper is irradiated, what happens to its properties after a certain time?
- Are the treatments N or V able to protect the paper *from* irradiation damage?
- Is the possible protective effect of N or V towards irradiation the same after ageing?
- What happens to the paper during irradiation when it is saturated with water? What is the effect of time on such a paper?

Measurement of chemical and physical properties of Whatman paper

For the Whatman Paper no.1, only the degree of polymerisation (DP), colour and infrared spectra were measured the latter two using the same methods as for the commercial paper. For DP we used the French Standard AFNOR NF 12 005 in cupri-ethylen-diamine.

Microbiological tests

The biological tests were performed only on the commercial paper. It was not considered necessary to repeat previous experiences already performed on the Whatman Paper[1].

Paper contamination with microbial stocks

For the biological test, cellulolytic fungi originating from two different sources, were used. The first type was taken from a photograph full of fungi colonies that had developed after an accidental water infiltration. The second type was taken from the surface of a rotten lemon. The spores of this mixed population of microscopic moulds mainly consisted of *Penicillium spp.* They were put in tap water containing a surface-active substance (*Tween 80*, 0.2 %). Spores were counted by microscope using a Burker's counting chamber, and the water was diluted down to the concentration of 5 x 10^5 per ml. The solution was then sprinkled with an atomiser onto the paper samples until they were completely saturated. The contaminated paper was kept for 15 days in daylight in a warm and damp environment (25°C 95% R.H.), imitating favourable conditions for the growth of micro-organisms. A non-contaminated set of samples was prepared too ("blank"). They were kept in plastic bags, under environmental conditions not favouring mould growth, to avoid any contamination by handling. The paper samples were exposed to N, S, V treatments and then irradiated at 2, 3 and 5 kGy.

Evaluation of the microbial load

The microbiological test was carried out on both the artificially contaminated and on the non-contaminated set of samples. From each sample, pieces 6 x 6 cm were obtained. Working sterilely and using the microorganisms on the paper itself (tampon technique), a first series of Petri dishes was seeded on a solid culture medium (yeast extract medium with 0.5 g/l of glucose, pH 4.5). The same samples of paper were subsequently incubated on the same solid culture medium in another series of Petri dishes. The incubation was performed at 30°C, for 10 days. After this period the microbial population was quantified by counting the colonies, on the culture-medium surface (first series of dishes) and directly on the paper (second series of dishes). The results are given as the average of 10 measurements (Table 12–14).

This method made the microbial population visible and therefore measurable. It also allowed the microbial populations that were present as quiescent spores to be detected, which could not be seen by visual examination.

The tests on the mechanical, optical and chemical paper properties, as well as the colour measurements, were performed at the laboratories of the Istituto Poligrafico e Zecca dello Stato. The tests on the polymerisation degree and the infrared measurements were performed at the Istituto Centrale per la Patologia del Libro. The Ente per le Nuove tecnologie, l'Energia e l'Ambiente performed the microbiological trials.

Table 1: Tensile strenght (kN m^{-1}).

		Machine direction						Cross direction					
		0 kGy		2 kGy		5 kGy		0 kGy		2 kGy		5 kGy	
		$\bar{X}$	T	$\bar{X}$	T	$\bar{X}$	T	$\bar{X}$	T	$\bar{X}$	T	$\bar{X}$	T
Unaged	Z	4.54	ab	4.37	abc	4.14	cdef	2.39	abcd	2.30	defg	2.31	bcdef
	N	4.16	cdef	4.46	abc	4.12	cdef	2.23	efgh	2.52	a	2.33	bcdef
	V	4.41	ab	4.34	abcd	4.32	abcd	2.12	h	2.43	abcd	2.38	abcde
	S	4.05	efg	3.94	fgh	3.61	ij	2.11	h	2.49	a	2.33	bcdef
Aged	Z	4.21	bcde	4.32	abcd	3.80	ghij	2.12	h	2.47	ab	2.21	fgh
	N	3.82	ghi	4.31	abcd	4.12	cdef	2.22	fgh	2.43	abcd	2.14	gh
	V	4.30	abcd	3.99	efg	4.00	efg	2.33	bcdef	2.30	cdef	2.08	h
	S	4.09	def	3.57	j	3.73	hij	2.46	abc	2.29	defg	2.18	fgh

$\bar{X}$ = average T = Tukey test

RESULTS: EFFECTS OF TREATMENTS ON THE PROPERTIES OF THE COMMERCIAL PAPER

Mechanical properties

The tensile strength of paper is directly correlated to the number and to the strength of links between the cellulose fibres. It decreases when moisture in the paper increases.

The decrease of tensile strength due to irradiation (Table 1) is considered to benegligible. Statistic tests have shown a significant difference only after a 5 kGy treatment and only for MD tensile strength. Also after accelerated ageing the irradiated papers did not show a reduction of their tensile strength, except only in the MD tensile strength of papers irradiated with 5 kGy. With the exception of CD tensile strength in the samples irradiated with 2 kGy and only for the treatment N, no relevant differences were noticed in the associated treatment. After ageing, the protection effect is shown by the treatment N, only for MD at 5 kGy dose. The irradiation of paper saturated with water caused a decrease of MD tensile strength and an improvement of the CD one. Nevertheless, after ageing, the irradiated papers S show a reduction of tensile strength in all cases.

The tearing resistance of the paper is a function of the length and flexibility of cellulose fibres. It increased with an increase in water content of the paper (Table 2).

Irradiation alone did not cause relevant variations of tearing resistance. Taking for granted that usually accelerated ageing causes a degradation of tearing resistance, it can be observed that only irradiation with 5 kGy caused a relevant worsening of such resistance after ageing. With reference to the treatment V, an

Table 2: Tearing resistance (mN).

		Machine direction						Cross direction					
		0 kGy		2 kGy		5 kGy		0 kGy		2 kGy		5 kGy	
		$\bar{x}$	T	$\bar{x}$	T	$\bar{x}$	T	$\bar{x}$	T	$\bar{x}$	T	$\bar{x}$	T
Unaged	Z	557	cd	545	cdef	530	defgh	587	fgh	601	defg	599	defg
	N	561	c	530	defgh	493	jk	595	defgh	581	fgh	573	ghi
	V	600	b	616	B	528	defghi	653	bc	681	ab	577	fgh
	S	661	a	538	cdefg	565	c	691	a	608	def	622	cde
Aged	Z	499	ijk	516	fghij	451	l	577	fgh	575	ghi	512	j
	N	549	cde	524	efghi	479	kl	593	efgh	563	hi	520	j
	V	506	hijk	510	ghij	512	ghij	581	fgh	626	cd	543	ij
	S	540	cdefg	518	fghij	557	cd	601	defg	589	fgh	602	def

Table 3: Folding endurance (Log10 n° double folds).

		Machine direction						Cross direction					
		0 kGy		2 kGy		5 kGy		0 kGy		2 kGy		5 kGy	
		$\bar{x}$	T	$\bar{x}$	T	$\bar{x}$	T	$\bar{x}$	T	$\bar{x}$	T	$\bar{x}$	T
Unaged	Z	1.909	bcde	1.791	efghi	2.025	ab	1.430	cde	1.394	de	1.534	abcd
	N	1.958	abcd	1.904	bcde	1.853	defg	1.474	bcde	1.571	abc	1.583	abc
	V	2.016	ab	1.749	fghij	1.967	abcd	1.646	ab	1.552	abcd	1.551	abcd
	S	2.060	a	1.793	efghi	1.988	abc	1.672	a	1.525	abcde	1.510	abcde
Aged	Z	1.784	efghi	1.758	fghi	1.740	ghij	1.420	cde	1.454	cde	1.437	cde
	N	1.670	ij	1.875	cdef	1.872	cdefg	1.458	cde	1.496	bcde	1.495	bcde
	V	1.939	abcd	1.842	defgh	1.624	j	1.472	cde	1.574	abc	1.199	f
	S	1.895	bcde	1.894	bcde	1.710	hij	1.502	abcde	1.501	abcde	1.359	ef

Table 4: Stretch at break (%).

		Machine direction						Cross direction					
		0 kGy		2 kGy		5 kGy		0 kGy		2 kGy		5 kGy	
		$\bar{x}$	T	$\bar{x}$	T	$\bar{x}$	T	$\bar{x}$	T	$\bar{x}$	T	$\bar{x}$	T
Unaged	Z	1.75	b	1.75	b	1.65	b	3.30	i	4.80	ab	3.90	efghi
	N	1.75	b	1.65	b	1.66	b	4.65	abcd	4.45	bcdef	3.76	ghi
	V	1.85	b	1.59	b	1.77	b	4.15	cdefg	3.65	ghi	4.05	defgh
	S	2.40	a	1.79	b	1.80	b	5.15	a	4.50	bcde	4.70	abc
Aged	Z	1.70	b	1.65	b	1.56	b	3.85	fghi	3.85	fghi	3.70	ghi
	N	1.70	b	1.65	b	1.65	b	3.90	efghi	4.15	cdefg	3.45	hi
	V	1.65	b	1.67	b	1.75	b	3.75	ghi	3.45	hi	3.80	ghi
	S	1.85	b	1.67	b	1.67	b	4.10	cdefg	3.80	ghi	4.15	cdefg

$\bar{x}$ = average T = Tukey test

Table 5: ISO brightness (%) and light absorption coefficient (%).

		ISO brightness (%)						Light absorption coefficient (%)					
		0 kGy		2 kGy		5 kGy		0 kGy		2 kGy		5 kGy	
		$\bar{x}$	T	$\bar{x}$	T	$\bar{x}$	T	$\bar{x}$	T	$\bar{x}$	T	$\bar{x}$	T
Unaged	Z	93.9	a	91.8	bc	90.2	d	0.645	l	0.843	ijk	0.962	hi
	N	93.8	a	91.7	c	89.7	d	0.711	jkl	0.860	ij	1.009	gh
	V	93.9	a	91.6	c	89.8	d	0.669	kl	0.865	ij	0.979	hi
	S	93.7	a	92.3	b	91.3	c	0.636	l	0.845	ij	0.917	i
Aged	Z	77.9	e	75.3	h	72.7	jk	1.474	de	1.728	bc	1.837	b
	N	77.8	ef	76.3	g	73.2	j	1.336	ef	1.520	d	1.784	b
	V	77.2	f	75.3	h	72.3	k	1.229	fg	1.599	cd	2.063	a
	S	77.3	ef	75.6	h	74.3	i	1.289	f	1.531	d	1.873	b

$\bar{x}$ = average T = Tukey test

improvement (restricted to the dose of 2 kGy) of this parameter was observed. After accelerated ageing, the treatment V seemed to have an improving effect, limited to MD at 5 kGy and to CD at 2 kGy. After accelerated ageing, treatment N did not seem to have synergetic effects. The irradiation of paper S caused a decrease of the tearing resistance in all cases. Nevertheless, after a certain time i.e. after accelerated ageing, such differences are not relevant.

Both folding endurance and the stretch at break of the paper depend, like tearing resistance, on the flexibility and length of the fibres.

The measured numbers (Table 3 and 4) do not bring new, relevant indications and the conclusions drawn from tearing resistance can also be applied to these two properties.

Optical properties

The diffuse blue reflectance factor (ISO brightness) is an aesthetic and not a functional aspect of the paper, but it is important for the readability of the document and for good reproduction of the tonal range of images. Its reduction does not necessarily mean a loss of mechanical qualities (Table 5).

Irradiation reduced the ISO brightness in a statistically relevant way, and this reduction is in correlation to the to the irradiation dose. After ageing the irradiated samples showed a greater reduction depending on the irradiation dose. Reduction caused by ageing is, in any case, greater than reduction caused by irradiation. Treatments N and V did not seem to influence the reduction of the ISO brightness. Treatment S increased the loss of ISO brightness in the irradiated

Table 6: Light scattering coefficient (%) and colour coordinate L* (%)

		Light scattering coefficient (%)						Colour coordinate L* (%)					
		0 kGy		2 kGy		5 kGy		0 kGy		2 kGy		5 kGy	
		$\bar{x}$	T	$\bar{x}$	T	$\bar{x}$	T	$\bar{x}$	T	$\bar{x}$	T	$\bar{x}$	T
Unaged	Z	48.36	abcd	48.37	abcd	47.51	abcd	93.0	ab	93.4	a	92.8	ab
	N	48.91	abc	48.19	abcd	47.80	abcd	93.0	ab	93.3	ab	92.8	ab
	V	47.77	abcd	47.76	abcd	47.55	abcd	92.7	ab	92.8	ab	92.9	ab
	S	45.11	cde	46.51	bcde	45.61	bcde	93.3	ab	93.0	ab	92.6	b
Aged	Z	51.32	a	48.97	abc	47.25	abcde	91.6	cd	90.8	efg	89.9	h
	N	48.23	abcd	46.74	bcde	46.58	bcde	90.9	cdefg	90.9	cdef	90.2	gh
	V	43.20	e	47.01	bcde	49.35	ab	91.6	c	90.9	defg	90.4	fgh
	S	46.82	bcde	44.65	de	46.44	bcde	91.3	cde	90.9	cdefg	90.2	fgh

$\bar{x}$ = average T = Tukey test

samples, both before and after ageing. ISO brightness reduction is less relevant in samples irradiated with 2 kGy in nitrogen atmosphere, and aged.

The light absorption coefficient is the measurement of the quantity of absorbed light when this crosses a layer of paper. Therefore, the increasing of such a parameter is an indication of the paper darkening, which is inversely correlated to the reflectance factor determined under various spectra conditions, as for instance the ISO brightness.

Irradiation increased, in a relevant statistical quantity, the light absorption coefficient (Table 5). Ageing, too, increases the light absorption coefficient. An interaction between irradiation and ageing was noticed. The treatments N and V did not show any effect on this parameter. When subjected to treatment N, the artificially aged samples showed a relatively small increase of this parameter, limited to the dose of 2 kGy. The irradiation of samples S increased the light absorption coefficient. This result is confirmed after ageing.

The light scattering coefficient is a measurement for the quantity of diffused light inside a paper layer when crossing it. In the graphic industry a high light coefficient is esteemed as a positive feature: a paper with high light scattering coefficient allows the better reproduction of images when its tonal range is considered. This parameter is an inverse function to the quantity of optical contact points between the fibres; this quantity decreases when the bonds between the fibres break (Table 6).

Neither irradiation nor ageing substantially modified the light scattering coefficient in a relevant way: this parameter can be higher or lower after irradiation and after ageing, and the differences are very small. Again, there is little difference between the Z-, N-, V- and S-treatments.

Table 7: Colour coordinate a* (%) and colour coordinate b* (%).

		Colour coordinate a* (%)						Colour coordinate b* (%)					
		0 kGy		2 kGy		5 kGy		0 kGy		2 kGy		5 kGy	
		$\bar{x}$	T	$\bar{x}$	T	$\bar{x}$	T	$\bar{x}$	T	$\bar{x}$	T	$\bar{x}$	T
Unaged	Z	0.62	abcd	0.50	cdefg	0.48	defg	-0.48	e	-0.36	e	-0.46	e
	N	0.58	bcdef	0.50	cdefg	0.42	efg	-0.38	e	-0.32	e	-0.48	e
	V	0.62	abcd	0.50	cdefg	0.40	fg	-0.52	e	-0.54	e	-0.14	e
	S	0.58	bcdef	0.36	g	-0.06	h	-0.28	e	-0.42	e	-0.58	e
Aged	Z	0.72	ab	0.66	abcd	0.70	ab	5.44	bcd	5.76	abcd	6.14	a
	N	0.80	a	0.58	bcdef	0.66	abcd	6.10	ab	5.84	abcd	6.00	abce
	V	0.76	ab	0.64	abcd	0.68	abc	5.56	abcd	5.32	d	5.92	abcd
	S	0.74	ab	0.60	bcde	0.60	bcde	6.16	a	5.42	cd	5.86	abcd

$\bar{x}$ = average T = Tukey test

Colour measurements

Colour is an aesthetic quality of paper that can be objectively estimated and can be expressed by the chromaticity co-ordinates L*, a* and b* of the CIE system (Comité Internationale de l'Eclairage): a* is the red-green axis in which red tonalities are in the positive field and green in the negative field; b* is the yellow-blue axis in which yellow tonalities are in the positive field and the blue in the negative field; L* is the lightness factor; L*=0 corresponds to the black and L*=100 to maximum white.

On the basis of the experimental values shown in Tables 6 and 7 it can be affirmed that:

- Irradiation alone does not statistically modify the colour of the commercial paper in a relevant way.
- Accelerated ageing, alone, causes statistically relevant colour variations to the co-ordinates L* and b*. If we compare the aged samples, a synergetic effect can be measured between ageing and irradiation in the direction of a slight, but statistically relevant, reduction of the co-ordinate L*.
- The treatments N and V, when associated to irradiation, do not show any effect either before or after accelerated ageing.
- The treatment S does not, generally, show relevant colour variations.

Chemical properties

The pH did not suffer at all from the various associated treatments. The Kappa number changed only after accelerated ageing when it increased, a well-known

Table 8: pH and Kappa number.

		pH			Kappa number		
		0 kGy	2 kGy	5 kGy	0 kGy	2 kGy	5 kGy
Unaged	Z= "open air"	9.18	9.40	9.11	2.96	2.78	2.40
	N= "Nitrogen"	9.30	9.25	9.17	3.12	3.17	3.11
	V= "Vacuum"	9.55	9.01	9.23	2.89	3.20	3.40
	S= "Saturated"	9.43	9.46	9.41	2.99	2.85	2.86
Aged	Z= "open air"	9.14	9.18	9.00	3.55	3.92	3.73
	N= "Nitrogen"	9.28	9.40	9.11	3.43	2.86	3.99
	V= "Vacuum"	9.35	9.11	9.31	3.19	3.73	3.95
	S= "Saturated"	9.48	9.11	9.40	3.23	3.59	3.10

phenomenon (Table 8). The statistical analysis related to chemical-physical and optical properties of commercial paper are summarised in Table 9. A discussion will be given in the Conclusions.

Effects of treatments on the properties of Whatman paper

Colour measurements

Table 10 shows the Whatman Paper L*, a* and b* colour co-ordinates. It can be observed that irradiation did not cause substantial reduction of the L* co-ordinate for the unaged samples. The aged samples, however, in comparison with the permanent paper, showed a small decrease of L* proportional to the irradiation doses. The b* co-ordinate increased proportionally with the irradiation of all samples: less so in the unaged (0.3–0.4 units) and by a more significant amount (ca. 2 units) in the aged samples. The a* co-ordinate was unchanged for the unaged samples, but it suffered a small increase (ca. 0.4 units) in the artificially aged samples.

On the whole, the Whatman paper had the tendency to yellow: such change of colour, visible also to the naked eye, is not lessened by any of the preliminary associated treatments.

Averaged viscometric degree of polymerisation (DP)

The viscometric measurement, which can be executed with reliability only on pure cellulose, allows an indirect evaluation of the length of the cellulosic macromolecule.

Table 9: Summary of statistical analysis

Measured parameters		Irradiation (kGy) general	0 vs 2	0 vs 5	2 vs 5	Pretreatments general	Z vs N	Z vs V	Z vs S	N vs V	N vs S	V vs S	Ageing
tensile	MD	••	n.s.	–	–	••	n.s.	n.s.	–	n.s.	–	–	••
strength	CD	••	+	n.s.	–	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	••
tearing	MD	••	–	–	–	••	n.s.	+	+	+	+	+	••
resistance	CD	••	n.s.	–	–	••	n.s.	+	+	+	+	n.s.	••
folding	MD	••	–	–	n.s.	••	n.s.	n.s.	+	n.s.	n.s.	n.s.	••
endurance	CD	••	n.s.	–	–	••	+	+	+	n.s.	n.s.	n.s.	••
stretch	MD	••	–	–	n.s.	••	n.s.	n.s.	+	n.s.	+	+	••
at break	CD	•	n.s.	–	–	••	n.s.	n.s.	+	–	+	+	••
ISO brightness		••	–	–	–	••	n.s.	–	+	–	+	+	••
Light absorption coeff.		••	+	+	+	••	n.s.	n.s.	–	n.s.	n.s.	–	n.s.
Light scattering coeff.		n.s.	n.s.	n.s.	n.s.	••	n.s.	–	–	n.s.	–	–	••
Colour co-ordinate L*		••	n.s.	–	–	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	••
Colour co-ordinate a*		••	–	–	–	••	n.s.	n.s.	–	n.s.	–	–	••
Colour co-ordinate b*		••	n.s.	n.s.	• +	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	••
Kappa number		n.s.				n.s.							n.s.
pH		n.s.				n.s.							

•: $\alpha = 0.05$

••: $\alpha = 0.01$

–: negative relevant difference for $\alpha = 0.05$

+: positive relevant difference for $\alpha = 0.05$

n.s. = not significant

Table 10: Colour measurements of Whatman Paper.

		0 kGy			2 kGy			5 kGy		
		L*	a*	b*	L*	a*	b*	L*	a*	b*
Unaged	Z = "open air"	96.0	0.0	0.5	95.5	0.0	0.5	95.8	0.0	0.8
	N = "Nitrogen"	96.2	0.0	0.5	95.7	0.0	0.5	95.9	0.0	0.9
	V = "Vacuum"	95.7	0.1	0.4	95.5	0.0	0.5	95.8	0.0	0.7
	S = "Saturated"	95.7	0.0	0.4	95.6	0.0	0.5	95.9	0.1	0.9
Aged	Z = "open air"	94.2	0.3	3.1	93.3	0.5	4.7	92.7	0.8	5.8
	N = "Nitrogen"	94.0	0.3	3.1	93.0	0.7	5.1	92.7	0.8	5.8
	V = "Vacuum"	94.0	0.3	3.1	93.9	0.4	4.1	93.2	0.7	5.4
	S = "Saturated"	94.2	0.2	3.2	93.9	0.3	4.1	93.6	0.4	4.8

Table 11: Viscometric degree of polymerisation of Whatman Paper. Retention = percentage compared with the non irradiated samples.

		0 kGy		2 kGy		5 kGy	
		DP	retention %	DP	retention %	DP	retention %
Unaged	Z = "open air"	1353	100	969	71	732	54
	N = "Nitrogen"	1300	100	986	75	733	56
	V = "Vacuum"	1366	100	1014	74	739	54
	S = "Saturated"	1218	100	980	80	721	59
Aged	Z= "open air"	1214	100	779	64	552	45
	N= "Nitrogen"	1231	100	780	63	538	43
	V= "Vacuum"	1226	100	789	64	575	46
	S= "Saturated"	1241	100	770	62	589	47

As previously observed[1] irradiation causes a depolymerization of cellulose in relation to the absorbed dose. The difference between the Whatman paper DP, which was irradiated and the Whatman paper DP which was not irradiated is also evident after accelerated ageing, always in relation to the absorbed dose. The various preliminary combined treatments did not cause substantial differences (Table 11).

FTIR MEASUREMENT

The FTIR spectroscopy is useful both for identification of extraneous components on the examined paper materials, and to appraise structural changes due to oxidation and other chemical processes [7-10]

The samples of Whatman Paper, analysed for this parameter, did not show differences, up to an irradiation of 5 kGy; the spectra are nearly identical (Fig. 1). Considerable differences out of experimental error become evident only with the application of *opportune spectra re-reading procedures*[11-14] and can be taken as an indication of the presence of unsaturated and structurally altered materials. Also, the spectra of the permanent paper samples, read as such or normalised at 1059 cm^{-1}, show only small differences, and can be taken as an indication of chemical changes in the polymer (Fig. 2).

The spectra of the permanent paper are characterised in the zone 2000-450 cm^{-1}, by substantial absorption due to other non-cellulosic components, prevalently calcium carbonate identifiable by the absorption at 1797, 1424, 876 and 713 cm^{-1}, and other substances mixed with polysaccarides, partly identifiable by opportune procedures, as alkyldiketenes, starches and azo-compounds. Such substances, es-

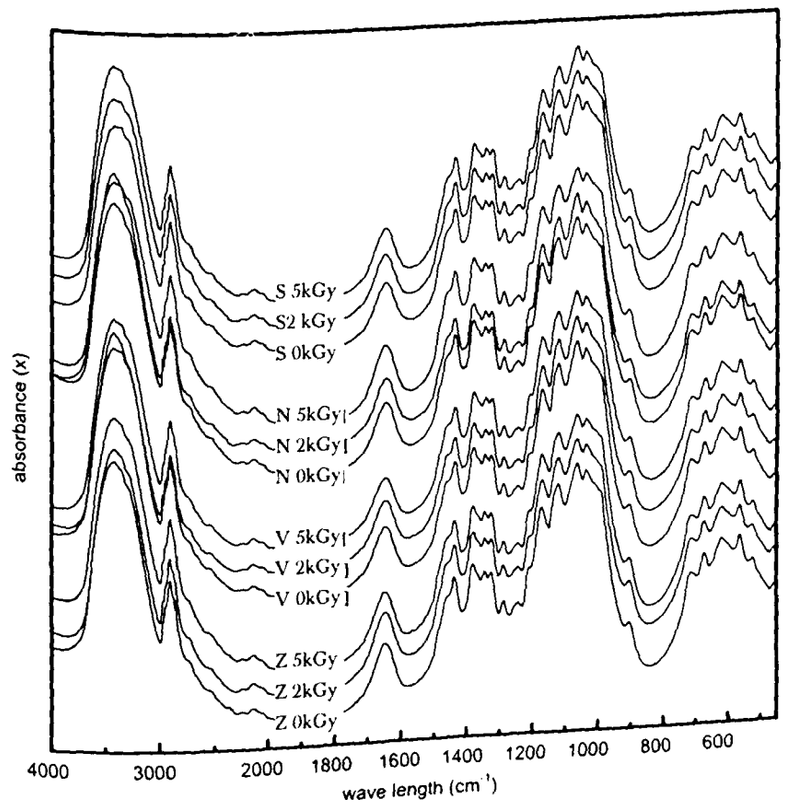

Fig. 1. Transmission FTIR spectra of irradiated and accelerated aged Whatman samples; all spectra in the stack picture are normalized at the same frequency.

pecially calcium carbonate, are so intimately tied up with the polysaccaridic component that they cause the deformation of the IR signal in a non linear way.

Both the curvefittings[14,15] and the other re-reading methods point out limited variations on the intensity of the absorption peaks and small shifts of the main frequencies due to the polysaccaridic chain, which can be attributed to variations of the amorphous-crystalline structure, and to the polymer-polymer and polymer components interaction parameters. Only the small variations verifiable in relationship to the frequency reference of 1220 cm^{-1}, attributed to the deformation of alcoholic groups[8], seem to suggest the breaking or the alteration of the intra ring bond C2-C3 without forming, however, consistent unsaturated quantities.

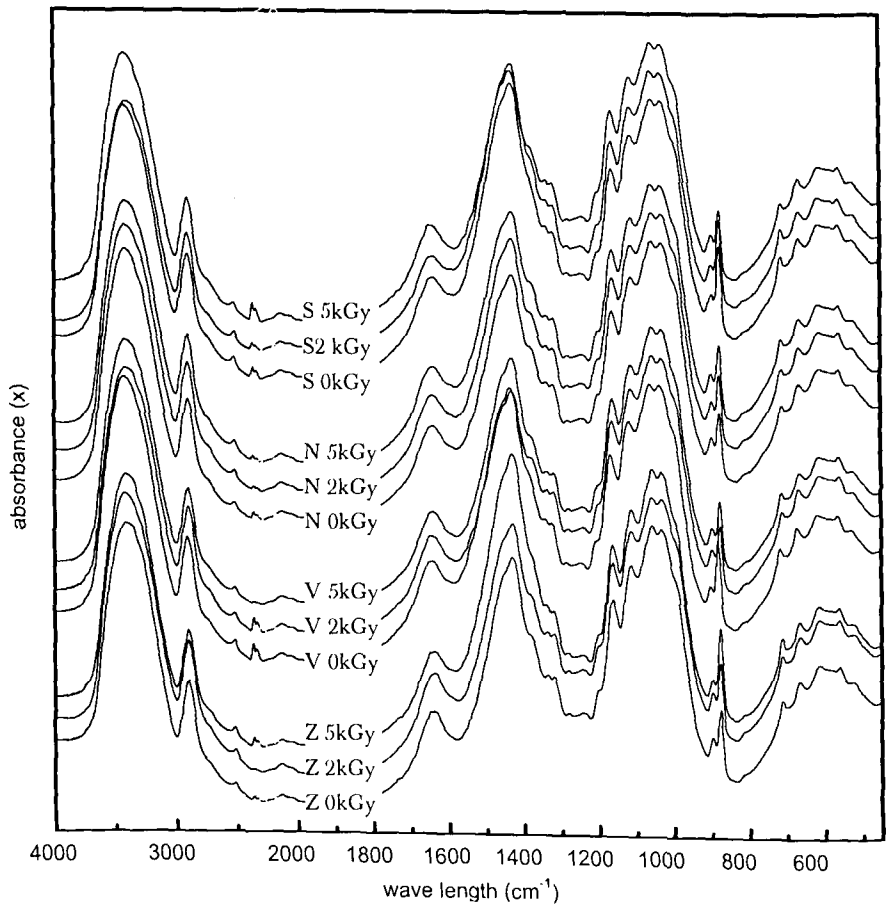

Fig. 2: Irradiated and accelerated aged permanent paper; the spectra in stack composition are all normalized at the same frequency.

This is confirmed by the smallness of the signal at 1735 cm^{-1} of carbonyl, carboxyl and aldehyde groups, and by the absence of absorption, at 1760–1780 cm^{-1}, due to lactonic components, frequently present in oxidised cellulose.

Efficiency of Treatments on the Microbial Population

Fig. 3 illustrates a series of paper samples as they appear after an incubation period under experimental conditions on an artificial culture medium. The development of the microbial flora is evident by coloured stains, more or less extended

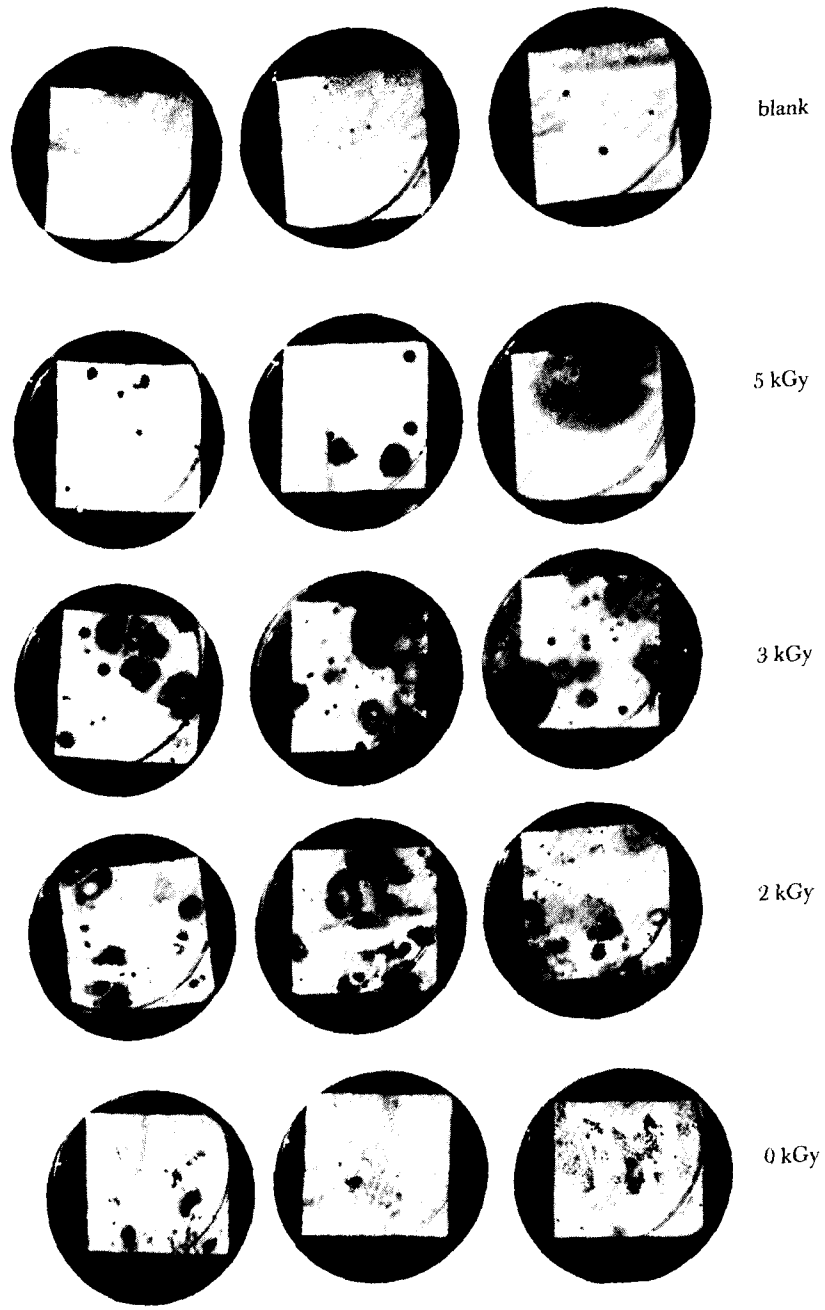

Fig. 3: Fungi colonies developed on paper samples.

Table 12: Number of fungi stains developed on paper samples; s = standard deviation.

	blank number	s	0 kGy number	s	2 kGy number	s	3 kGy number	s	5 kGy number	s
Z = "open air"	5.60	2.80	*		54.60	8.30	46.80	13.70	12.60	4.60
N = "Nitrogen"	3.80	1.30	36	9.60	3.50	2.00	0.37	0.60	0.37	0.60
V = "Vacuum"	0.62	0.49	>96	32.0	70.20	29.70	4.50	1.30	8.0	3.00
S = "Saturated"	2.12	2.00	58.50	17.20	5.60	1.60	4.00	1.50	0.12	0.30

* not measurable because number of fungi stains was too high

Table 13: Number of fungi colonies developed on agar: average and standard deviation.

	blank number	s	0 kGy number	s	2 kGy number	s	3 kGy number	s	5 kGy number	s
Z = "open air"	4.10	1.6	127	20	18.80	6.3	5.20	1.6	2.50	2.2
N = "Nitrogen"	9.00	5.3	373	45.9	1.00	1.3	0.00	-	0.00	-
V = "Vacuum"	1.25	3.5	>155	28.0	32.80	21.9	2.70	2.5	5.10	2.1
S = "Saturated"	1.57	0.5	65.1	18.8	2.00	2.3	1.50	2.1	0.12	0.3

Table 14: Percentage of fungi colonies compared with the non irradiated samples (0 kGy).

	blank	2 kGy	3 kGy	5 kGy
Z = "open air"	3.22	14.8	4.09	1.96
N = "Nitrogen"	2.41	0.26	-	-
V = "Vacuum"	<0.8	<21.1	<1.74	<3.29
S = "Saturated"	2.4	3.03	2.30	0.18

or numerous, according to the species used and to the depleting effect of the treatment.

Table 12 gives the average number of these stains. It must be emphasized that the number of stains of microbial origin on the paper is not identical with the whole of the microbial population to be found on the same samples of paper. Table 13 gives the average number of microbial colonies developed in the microbiologially contaminated Petri dishes. Table 14 and Fig. 4 give their percentages compared to the value of the control sample (0 kGy = not irradiated). A clear effect of gamma radiation in eliminating the fungous microflora is evident. It is proportional to the dose absorbed by the examined material.

With regard to the results of the treatments associated to irradiation, it must be specified that under the described experimental conditions

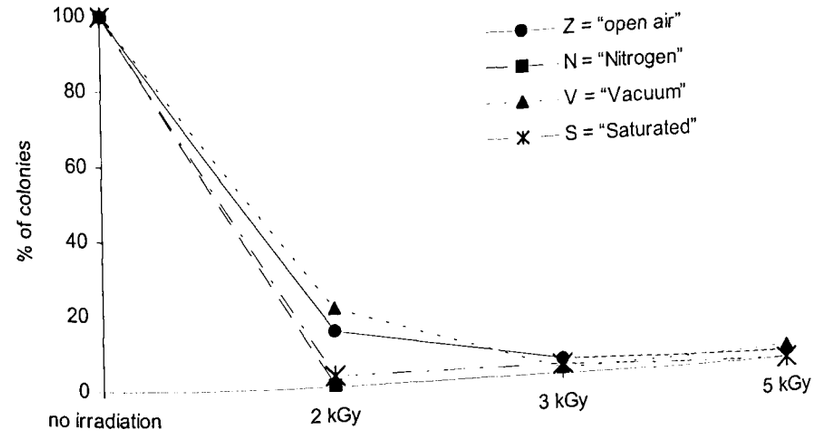

Fig. 4. Trend of fungi colonies in function of the irradiation dose and associated treatment

- the values of the samples treated under vacuum (V) are all inferior, in their absolute value, if compared with the analogous treatments carried out in room atmosphere,
- the samples treated in an atmosphere saturated with nitrogen (N) seem, instead, to not be at all influenced by this treatment; some results are even contrary to the expectations,
- the values of the samples irradiated under extremely damp conditions (S) show clearly the effect of water in elevating the germicidal power of radiation.

CONCLUSIONS

We concluded from our experiments that an irradiation dose of 5 kGy caused statistically significant variations on almost all the paper properties. The treatment at 2 kGy, however, does not induce, in many cases, statistically significant modifications of the commercial paper.

Generally, the vacuum (V) and the nitrogen (N) treatments did not reduce the negative effects of irradiation upon paper. As we expected, the S treatment modifies the paper properties. In fact, S samples have a moisture content higher than the Z samples when in equilibrium with the conditioning atmosphere (23° C 50% RH).

These results were not surprising, as they were in accordance with the cellulose hygrometrical hysteresis[16]. Higher moisture content decreases the tensile strength while improving the stretch at break, the tearing resistance and the folding endurance.

In the experiments with the accelerated aged samples it is impossible to reproduce exactly the effects of natural ageing. Nevertheless, the accelerated ageing method proved to be useful when investigating the effects of irradiation and the associated treatments on paper properties. Accelerated ageing usually causes a decrease of those mechanical properties that depend on fibre length and flexibility (tearing resistance, folding endurance). On the other hand, heat can increase the interfibre bonds and therefore the paper properties, depending on these bonds, can improve (tensile strength, bursting resistance). Unfortunately, the artificially aged paper gave quite variable results when tested: all considerations concerning the ageing effect are therefore subject to a certain error[17,18].

The colour of commercial paper was resistant to irradiation. Accelerated ageing caused the well-known yellowing effect in all samples. After ageing, the samples irradiated at 5 kGy showed a slight decrease of L* with respect to non-irradiated samples, suggesting that the effect of irradiation becomes visible only over time. Only after accelerated ageing and with an irradiation dose of 5 kGy the lightness (L*) slightly decreased. Nevertheless, this colour modification could not be detected by visual examination. The irradiated Whatman Paper showed a slight tendency to yellowing after accelerated ageing.

The viscometric degree of polymerisation of Whatman Paper confirmed, as previously observed[3], the depolymerising effect of gamma rays on cellulose. Depolymerisation occurs also after ageing, with a synergetic effect when associated to an irradiation treatment. The cellulose depolymerisation, however, caused by the low doses of irradiation which are sufficient for paper recovery, is still acceptable if we consider that this treatment would be used for paper materials already seriously infected. The advantage of irradiation with respect to other disinfectant treatments is that it does not leave behind any harmful residue, so that the subsequent handling of the documents is free of hazards.

From the spectra obtained for Whatman Paper, some small oxidation differences are quantified spectrometrically in a maximum of 5% of CO mmol/g^{-1}. The commercial paper, which is characterised by substantial signals of calcium carbonate, (content esteemed at 10–15%), shows after the treatment some small spectra differences, especially in the CHs and aldehydic groups, 2900 and 1360 cm^{-1}, and in the alcoholic groups stretching zone, 1220 cm^{-1}, that seem to point out to the prevalence of depolymerization compared to oxidation[19]. In fact, in the oxidised groups zone, 1735 cm^{-1}, no absorption with a percentage of CO higher than those determined for Whatman paper are found, even in curve-fitting and Fourier de-

convolutions. The small modifications in the commercial paper spectra are principally due to depolymerization and to the change of the relationship between its amorphous and its crystalline structure. These spectral changes can also be ascribed to the interactions between polysaccharides and other components. The very limited variations observed in Whatman Paper spectra are due to the polysaccharide skeleton rearrangements, as also indicated by absorption signals at 1430 and 900 cm^{-1} [20, 21]. IR observations show that the studied papers do not show substantial structural changes and that the various associated treatments seem to have an irrelevant influence on the irradiation effects.

The increase of the kappa number and of the light absorption coefficient, proportional to the absorbed dose, can be related to the DP decrease. Accordingly, the ISO brightness and the light scattering coefficient decrease when paper is irradiated, even if this is slight.

The whole set of results on the fungi population survival clearly indicates that the gamma radiation effects are proportional to the absorbed dose. It is interesting to observe, that relatively low irradiation doses (2–3 kGy) decontaminate a paper, until the microbial presence reaches levels comparable, or even lower, to those found on the "blank" samples. This data seems to satisfy fully the objectives of a decontamination treatment. Such a treatment should not aim at a complete sterilisation of the contaminated material, which is not even necessary[22], but at the removal of biodeteriogenous micro-organisms when they are too many, because of anomalous environmental situations.

In the treatment of paper saturated with water (S-samples), a synergetic effect of the water during the irradiation phase can be observed. This may be explained by considering that when water is irradiated, free short-lasting radicals develop which have a germicidal power, added to the irradiation germicidal effect. For the other associated treatments (V = "Vacuum", N = "Nitrogen"), related to the absence of oxygen, the observed differences are negligible; they cannot justify an additional treatment. The differences in the microbial loads, also found at the same absorbed dose, can be caused by an accidental contamination, which may have occurred during the preparation of samples for the N and the V treatment, rather than to the effects of the treatments themselves. In fact, we have to keep in mind that for the V treatment it was necessary to create a vacuum, drawing out the air from bags containing contaminated paper samples. Similarly in the N treatment it was unavoidable to further disturb the environment, even if this should be avoided in microbiological experiments.

Altogether it can be stated that irradiation does not damage the mechanical properties of paper, while it can perform a drastic reduction of the biological agents responsible for the material deterioration: not only microscopic fungi as those studied in this work, but above all insects which are more sensitive to radia-

tion[2]. Nevertheless, before applying irradiation technology on a large scale for the recovery of damaged paper materials kept in libraries and archives, we intend in the future to make a more in depth study of the costs/benefits ratio for this technology with particular attention to the economical and engineering aspects. The advantage of irradiation with respect to other disinfectant treatments is that it does not leave behind any harmful residue, so that the subsequent handling of the documents is free of hazards.

It is necessary to remember that when irradiation treatment will be used on books and paper documents to prevent their degradation, a carefully considered evaluation about the choice of the technologies of intervention[22] will have to be done and it will be necessary to take care of other factors instead of only the material's answer to the treatment. Between these factors the following are decisive: the available alternatives, the entity and the typology of the biological attack, the urgency of intervention, the historical and commercial value of the material to be treated, the quantity, the economic and environmental costs of the treatment.

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SUMMARIES

Gamma Radiation Treatment of Paper in Different Environmental Conditions

A multidisciplinary team studied the effects of a decontaminating treatment with gamma radiation applied to a paper, which had been damaged by microscopic cellulosolytic fungi (mildews). Special attention was paid to the potentially negative effects of gamma rays on cellulose. The investigation was extended to the effects of some associated environmental treatments, such as the absence of oxygen and water saturation. The mechanical, chemical, physical and microbiological tests confirmed well-known observations already published. They indicated that the microbial population decreases proportionally to the gamma rays dosage together with the depolymerisation of the cellulose molecule. Nevertheless, this negative effect does not significantly affect the basic properties of a good printing paper. A correct analysis of costs and benefits would suggest the use of a dose of 2–3 kGy. However, this analysis has still to be further investigated for the practical application of irradiation on deteriorated books and documents.

Traitement au moyen de radiation gamma sur le papier en différents conditions de l'ambient.

Un groupe de travail pluridisciplinaire a étudié les effets d'un traitement de décontamination aux rayons gamma appliqué à un papier qui avait été endommagé par des microorganismes fongiques (moisissure). Une attention toute particulière a été accordée aux effets potentiellement négatifs des rayons gamma sur la cellulose. La recherche a également porté sur les effets associés de certains facteurs environnementaux, tels que l'absence d'oxygène et la saturation d'eau. Les analyses mécaniques, chimiques, physiques et microbiologiques confirment les observations antérieures bien connues et déjà parues dans des publications. Elles ont mis en évidence que la population microbienne décroît proportionnellement à la dose de rayons gamma administrée et qu'en même temps une dépolymérisation de la molécule de cellulose se produit. Néanmoins, cet effet négatif n'affecte pas de façon significative les propriétés fondamentales d'un papier de bonne qualité. Une analyse exacte des coûts et des bénéfices recommanderait l'utilisation d'une dose de 2–3kGy. Des analyses plus approfondies s'imposent cependant avant de passer à l'application pratique du traitement aux rayons gamma sur des livres et documents endommagés.

Die Gammabestrahlung von Papier bei verschiedenen Umweltbedingungen

Die Wirkung einer Desinfektiion von Papier, das von cellulolytischen Mikroorgasnismen (Schimmel) befallen ist, durch Gamma-Strahlen wurde von einem interdisziplinären Team untersucht. Besondere Aufmerksamkeit galt der eventuellen negativen Wirkung von Gammastrahlen auf Cellulose. In die Untersuchung wurden auch bestimmte umweltbedingte Gegebenheiten einbezogen, wie die Abwesenheit von Sauerstoff und die Feuchtesättigung des Papiers. Die mechanischen, chemischen, physikalischen und mikrobiologischen Untersuchungen bestätigten bereits früher publizierte Beobachrtungen und zeigten auf, daß das Ausmaß des mikrobiologischen Befalls wie auch der Polymerisationsgrad der Cellulose proportional zur Strahlendosis zurückgeht. Der negative Nebeneffekt hat aber keinen nennenswerten Einfluß auf die wesentlichen Eigenschaften eines guten Druckpapiers. Eine genaue Kosten-Nutzen-Analyse dürfte eine Dosis von 2–3 kGy als sinnvoll ergeben. Hierzu besteht jedoch weiterer Forschungsbedarf.

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M. Adamo, G. Magaudda
Ente per le Nuove Tecnologie l'Energia e l'Ambiente (ENEA)
Via Anguillarese 301,
S. Maria di Galeria
I-00060 Roma
Italy
Tel.: 39 6 30484629,
Fax.: 39 6 30484875

G. Martinelli
Istituto Centrale per la Patologia del Libro (I.C.P.L.)
Via Milano 76
00184 Roma
Italy

M. Brizzi, F. Rocchetti, F. Savagnone
Istituto Poligrafico e Zecca dello Stato (IPZS)
Piazza G. Verdi 10
00198 Roma
Italy

M. Plossi-Zappalà
Retired, formerly Director of Chemical Laboratory of
Istituto Centrale per la Patologia del Libro, Rome
Present professional address:
Università degli Studi di Udine
Via Antonini, 8
33100 Udine
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