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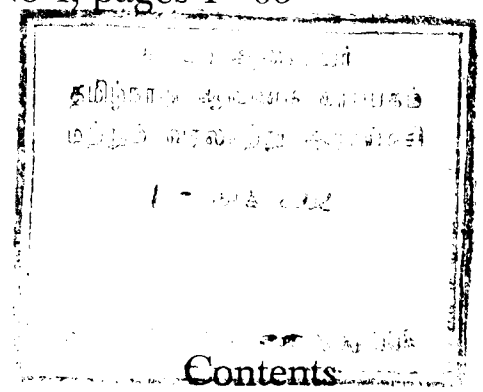

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Characterization of Foxing Stains by Chemical and Spectrometric Methods

by MARINA BICCHIERI, GIUSEPPE PAPPALARDO, FRANCESCO PAOLO ROMANO, FRANCESCA MARIA SEMENTILLI & RODOLFO DE ACUTIS

INTRODUCTION

Foxing, a recognisable chromatic alteration of cellulosic materials, is a complex phenomenon, not yet well understood. Its formation mechanisms have been studied since 1935. However, despite more recent intensive research since the 1980s there are still no conclusive results.

Foxing is the term applied to stains of reddish-brown, brown, or yellowish colour, generally of small dimensions, with sharp or irregular edges, most of which, if excited with UV light, show fluorescence. Fluorescence is also often present in areas in which the alteration is not yet visible under natural light, but which is probably in formation. According to the different morphologic and chromatic characteristics and the different fluorescence that the stains show when exposed to UV light Carter[1] defined four classes of foxing (Table 1) and Cain and Miller[2] defined five classes (Table 2). The fourth class in Cain and Miller's classification is due, in our opinion[3], to the oxidation of oils used in the typographic inks.

Gallo and co-workers[4] found evidence of bacterial and fungal stains in some foxed areas sometimes associated with the presence of iron. Other researchers[5] pointed out that the presence of this metal could favour the formation of foxing since iron can produce rust, due to the water content of paper, and induce the degradation of cellulose and other materials, such as sizing agents. Arai and co-workers[6, 7] supposed that foxing could be connected to the hydrolysis induced by fungal growth in cellulose and gelatine (in the case of gelatine sized papers). In fact, the products of hydrolysis, free sugars and amino acids, may combine to produce fluorogenic compounds and then chromogenic end products, responsible for the coloured stains, through a step process.

The hypothesis that foxing is a process developing through different steps was given also by Choisy and co-workers[8], who grouped their foxed samples in three categories, considering each one not as a separate phenomenon, but as three suc-

Table 1: Foxing classes by Carter.

Class	Appearance in natural light	Appearance in UV light
1	Yellow, orange or reddish-brown stains with well defined edges.	Reddish-black.
2	Stains with faded edges of dull orange-brown.	Not fluorescent, while the paper surrounding the stains is fluorescent.
3	Stains similar to type 2 but with a darker nucleus and a lighter edge.	The stain edge has a white fluorescence.
4	Pale yellow stains.	The stains appear bigger and have a white fluorescence.

Table 2: Foxing classes by Cain and Miller.

Type	Appearance in natural light	Appearance in UV light
1	Stain with black nucleus and concentric rings	Brown black with a yellow orange ring or not fluorescent.
2	a) Light brown stains, not nucleated with irregular edges.	White or pale yellow uniform fluorescence.
	b) Like stain 2a but lighter in colour. They could represent a further stage of the development of type 2a.	Same appearance as 2a
3	Stains spread all over the sheet, identical, in shape and colour, to the stains present on the sheet with which they are in contact.	Pale blue or white.
4	The typographic composition is included in a slightly larger stain.	The text is immersed in a yellow-orange fluorescence or in a yellow fluorescence.
5	Areas clearer than the surrounding paper.	Irregular shaped fluorescent white areas.

cessive steps of the same. They assumed that in the first step fluorogenic compounds appear, then chromogenic compounds in conjugated chromophores and that finally full colour is reached with free ketones.

EXPERIMENTAL

Method

We decided to analyze some foxed stains present on naturally aged papers from the 16th to 18th centuries, trying to find a common trend. We also prepared some

samples in which we induced the appearing of foxing stains on a modern paper (*Umbria* paper), after artificial ageing (15 days at 80°C, 65% RH). We used $5 \cdot 10^{-3}$ M solutions of $FeCl_3$ and KCl and we added, in restricted areas, 1, 3 and 5 µl respectively of $FeCl_3$, KCl and $FeCl_3$+KCl. We applied non-destructive and, when it was possible, destructive techniques to carry out a more complete analyses.

Materials

- Sample 1: paper from a manuscript of the second half of the 17th century
- Sample 2: paper from a manuscript of the first half of the 16th century
- Sample 3: printed paper from the second half of the 18th century
- Sample 4: printed paper from the second half of the 17th century
- Sample 5: printed paper from the second half of the 17th century
- Sample 6: printed paper from the second half of the 17th century
- Sample 7: *Umbria* paper, unprinted, treated with 1, 3 and 5 µl of $5 \cdot 10^{-3}$ M $FeCl_3$ solution.
- Sample 8: *Umbria* paper, unprinted, treated with 1, 3 and 5 µl of $5 \cdot 10^{-3}$ M KCl solution.
- Sample 9: *Umbria* paper, unprinted, treated with 1, 3 and 5 µl of $5 \cdot 10^{-3}$ M $FeCl_3$+KCl solution ($2.5 \cdot 10^{-3}$ M in $FeCl_3$ and $2.5 \cdot 10^{-3}$ M in KCl).

Measurements

Samples 1, 2 and 3 and 7, 8, 9 were fully tested. It was possible, in fact, to carry out destructive measurements; for the other samples only non-destructive techniques were employed, except for IR analysis of some foxed stains in sample 4. We analyzed:

- Sizing agents;
- fibre composition;
- average viscosity degree of polymerisation;
- pH;
- chromaticity co-ordinates;
- appearance under UV illumination;

- carbonyl groups content;
- thickness of paper.

For a fuller analysis we employed also:

- IR spectroscopy
- XRF spectrometry.

Some samples were treated with borane tert-butylamine complex, a reducing compound[9–12], to test its effectiveness in bleaching foxed areas. Borane tert-butylamine complex is able to react with carbonyl groups and partially with carbon-carbon double bonds.

RESULTS

Sizing agents

Before the advent of synthetic adhesives, the most commonly used products in paper manufacture were starch, gelatine and casein, the latter being especially used in the 20th century.

We tested the presence of starch exploiting the reaction between amylose and iodine that leads to the formation of a blue complex. Starch was found only on Sample 3 and in the *Umbria* paper. In the other samples we searched for proteinaceous substances. The test is based on the reaction between p-dimethylaminobenzaldehyde and hydroxyproline, obtained by alkaline hydrolysis of collagen. The specific colorimetric reaction relies on the oxidation of hydroxyproline to pyrrole and subsequent formation of a red-pink complex between pyrrole and p-dimethylaminobenzaldehyde. Other nitrogenous materials do not interfere with this test which, in this case, gave positive results for samples 1, 2, 4, 5 and 6 (Table 3).

Table 3: Composition of the samples.

Sample	Lignin	Fibres	Size	DP	DP after reduction	pH
1	–	linen, hemp and cotton (ca. 5%)	gelatine	80 ± 5	106 ± 10	3.08 ± 0.02
2	–	linen and cotton (ca. 20%)	gelatine	248 ± 25	269 ± 28	5.82 ± 0.02
3	–	linen and cotton (ca. 10%)	starch	416 ± 30	429 ± 30	6.50 ± 0.02
4, 5, 6	–	linen, hemp and cotton (ca. 60%)	gelatine	–	–	5.65 ± 0.02
7, 8, 9	–	cotton 34%, cotton linters 66%	starch	1179 ± 32	–	6.71 ± 0.02

Fibre composition

Identification of the fibre composition occurred after the paper had been kneaded and microscope slides, stained with suitable reagents, have been prepared for observation. A preliminary test on the lignin content (absent in all the studied samples) was performed to choose the most suitable stain. The Herzberg stain was used and the results obtained after microscopic observation are reported in Table 3.

Average viscosity degree of polymerisation

The average viscosity degree of polymerization, DP_v, related to the intrinsic viscosity $[\eta]$ of the papers, were obtained from Mark-Houwnik equations:

$$(1) \qquad [\eta] = K\overline{M}_v^{\alpha} \qquad\qquad (2) \qquad [\eta] = K'\overline{DP}_v^{\alpha}$$

The measurements of $[\eta]$ were carried out in accordance to ASTM 1795-90 Method. Results are reported in Table 3.

pH of the paper

For samples 1 to 3 and 7 to 9 we measured pH using the hot extraction method. On the other samples, that could not be destroyed, we measured only the surface pH. Results are reported in Table 3.

Chromaticity co-ordinates

If two specimens have the same values of chromaticity co-ordinates, they are of the same colour; conversely if any co-ordinate value is different, the overall difference is a measure of the perceived colour difference between them.

We choose to use the L*a*b* colour space in which a vertical axis (L*) has the black (L* = 0) at the bottom and the white (L* = 100) at the top. The two other axis, a* and b*, represent the green-red axis (from -a* to +a*) and the blue-yellow axis respectively (from -b* to +b*). Each colour is a point in the three-dimensional space defined by L*a*b* co-ordinates. An increase of L* increases the luminosity of the colour; an increase of b* shifts the tint to yellow whereas its decrease

means that the colour contains less yellow than before. The a* co-ordinate acts on the green-red axis, an increase of a* shifts to the red, a decrease to the green.

Results for the studied samples are reported in Tables 4 and 5.

Appearance under UV illumination

Foxed spots were observed under UV illumination at two wavelengths: 365 and 254 nm. Different kinds of fluorescence were noted in all the samples, these were more intense when 365 nm wavelength was used:

- Sample 1: White fluorescent points, not localised on the foxed spots, were dispersed all over the paper.
- Sample 2: Foxed areas were not fluorescent, while the not foxed areas had a yellow-orange fluorescence.
- Sample 3, 4, 5, and 6: All spots fluoresce pale yellow.
- Sample 7: The spots appeared bigger under UV illumination than in visible light: the brown areas, which were not fluorescent, were surrounded by a white fluorescent ring. The diameter of this ring is proportional to the quantity of iron added to the paper.
- Sample 8: The spots appeared pale white in visible light; under UV illumination the centre of the spot appeared slightly yellow and fluorescent while the halo was white and fluorescent.
- Sample 9: The brown spots, under UV illumination, were fluorescent and darker than in visible light. They appeared surrounded by a yellow-orange fluorescent ring.

When potassium ions were added onto the paper, they seemed to migrate from the centre of the spot to the external margin, giving rise to a ring around the application point. When iron and potassium ions were applied together, the iron migrated less than potassium. Potassium ions were localised especially on the margin of a circle the diameter of which was about twice as big as that of the iron spot.

Carbonyl content

The carbonyl content in the paper samples was detected using 2,3,5-triphenyl-2H-tetrazolium chloride (THTCl). Dissolved in water this compound forms a

Table 4: L*a*b* co-ordinates before and after reduction and washing.

		L*		a*		b*	
	treatment:	before	after	before	after	before	after
sample 1							
no foxing	reduction	53.2 ± 1.0	63.8 ± 0.2	7.2 ± 0.4	3.8 ± 0.1	19.9 ± 0.3	18.4 ± 0.2
foxing	reduction	52.5 ± 1.0	61.5 ± 1.0	7.3 ± 0.3	4.5 ± 0.1	22.1 ± 0.2	19.8 ± 0.2
no foxing	washing	50.2 ± 1.0	50.7 ± 1.7	7.5 ± 0.3	6.8 ± 0.2	20.3 ± 0.3	19.8 ± 0.4
foxing	washing	30.1 ± 1.7	30.4 ± 1.4	8.0 ± 0.4	7.8 ± 0.3	18.2 ± 0.2	18.2 ± 0.2
sample 2							
no foxing	reduction	64.9±1.0	78.7±0.3	5.6±0.3	3.2±0.1	17.1±0.3	15.0±0.2
foxing	reduction	52.8±1.8	62.6±1.8	8.9±0.5	6.9±0.5	21.8±0.7	20.5±1.0
no foxing	washing	66.1± 0.9	68.3±0.9	5.6±0.3	5.1±0.2	17.1±0.3	16.7±0.3
foxing	washing	57.9±1.2	59.7±1.4	7.2±0.5	6.9±0.2	19.5±0.7	19.4±0.4
sample 3							
no foxing	reduction	79.1 ± 1.2	82.7 ± 2.3	2.6 ± 0.3	3.2 ± 0.6	12.7 ± 0.5	12.5 ±0.7
foxing	reduction	61.4 ± 3.0	76.1 ± 1.4	5.0 ± 0.7	3.0 ± 0.3	17.6 ± 1.3	13.4 ± 0.7
no foxing	washing	75.7 ± 0.9	79.9 ± 3.3	3.4 ± 0.2	2.6 ± 0.6	13.7 ± 0.4	11.8 ± 0.7
foxing	washing	69.4 ± 2.2	72.8 ± 3.9	4.6 ± 0.6	3.6 ± 1.2	16.4 ± 1.5	13.8 ± 2.7

Table 5: L*a*b* co-ordinates before and after treatment with $FeCl_3$ and/or KCl solutions.

sample		treatment:	L* –	L* 1 µl	L* 3 µl	L* 5 µl	a* –	a* 1 µl	a* 3 µl	a* 5 µl	b* –	b* 1 µl	b* 3 µl	b* 5 µl
7, 8, 9	no foxing	none	92.3 ±0.3				0.3 ±0.1				7.0 ±0.3			
7	foxing	$FeCl_3$		89.1 ±0.4	88.4 ±0.5	87.9 ±0.4		1.0 ±0.1	1.2 ±0.1	1.3 ±0.1		10.3 ±0.6	11.7 ±0.4	12.2 ±0.2
8	light stain	KCl		91.6 ±0.3	91.5 ±0.5	91.7 ±0.4		0.2 ±0.1	0.3 ±0.1	0.2 ±0.1		7.1 ±0.2	7.1 ±0.1	7.0 ±0.2
9	foxing	$FeCl_3$ + KCl		90.6 ±1.0	88.8 ±0.3	88.7 ±0.3		0.5 ±0.1	0.9 ±0.1	1.1 ±0.1		8.7 ± 0.7	10.6 ±0.1	11.2 ±0.1

colourless solution. After reaction with mild reducers, such as C=O groups in cellulose, a red water-insoluble formazan is formed. The amount of formazan obtained is proportional to the quantity of reducing groups. When the time, temperature, alkalinity and water content of the solution are controlled, the redox reaction between THTCl and reducing groups can be used for a colorimetric measurement, after formazan dissolution in ethyl alcohol. The determination of

Table 6: Carbonyl content of treated and untreated samples.

sample		treatment:	m.moles C=O in g 100 of paper none	reduction	1 µl	3 µl	5 µl
1		–	40.5 ± 0.8	18.5 ± 0.6	–	–	–
2		–	32.8 ± 1.6	15.9 ± 0.8	–	–	–
3		–	16.9 ± 0.9	8.9 ± 0.4	–	–	–
7	no foxing	–	3.8 ± 0.1	–	–	–	–
7	foxing	$FeCl_3$	–	–	4.5 ± 0.3	4.7 ± 0.2	4.9 ± 0.2
8	no foxing	–	4.0 ± 0.1	–	–	–	–
8	light stain	KCl	–	–	5.0 ± 0.1	5.0 ± 0.1	5.2 ± 0.1
9	no foxing		3.9 ± 0.1	–	–	–	–
9	foxing	$FeCl_3$ + KCl	–	–	4.1 ± 0.1	4.0 ± 0.2	3.9 ± 0.2

Table 7: Thickness of treated and untreated samples.

sample	treatment:	thickness (µm) none	reduction	1 µl	3 µl	5 µl
1		193 ± 16	188 ± 11	–	–	–
2		120 ± 9	120 ± 6	–	–	–
3		129 ± 10	129 ± 8	–	–	–
4		131 ± 10	–	–	–	–
5		128 ± 9	–	–	–	–
6		133 ± 11	–	–	–	–
7	$FeCl_3$	235 ± 8	–	240 ± 10	227 ± 6	250 ± 10
8	KCl	220 ± 5	–	230 ± 8	230 ± 4	230 ± 7
9	$FeCl_3$ + KCl	210 ± 5	–	221 ± 4	207 ± 10	214 ± 8

carbonyl amount was performed as reported in a previous work[13]. Results are shown in Table 6.

Thickness of paper

Measurements were carried out on all the samples, before and after reduction (when the paper was submitted to this treatment). On samples 7–9, where the foxed zones were large enough, we also measured the thickness of areas which were both foxed and those which were not foxed. Results are reported in Table 7.

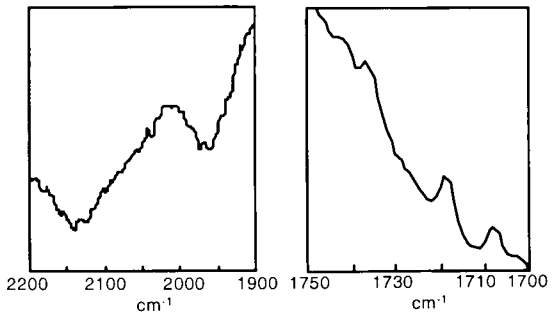

Figure 1: Sample 1, foxing spot; spectral regions 2200-1900 cm^{-1} and 1750-1700 cm^{-1}.

IR spectra

FTIR spectra of samples dispersed in KBr pellets were collected from areas that were foxed and those that were not damaged, in order to highlight and characterize degradation compounds, responsible for foxing. FTIR spectra, when possible, were also collected on reduced papers.

Attribution of bands is not very easy because different structures can coexist[14] in the same part of paper, unmodified, differently oxidized cellulose, hydrocellulose, etc. The following discussion of data reports only the most significant peaks. All peculiar bands of pure cellulose FTIR spectrum in fact have been omitted, to underline the peaks related to the degradation products.

Sample 1

The spectra were characterized by the peaks related to the stretching of carbon-carbon triple bonds (C≡C) at 2146 cm^{-1}, 2136 cm^{-1} and 2139 cm^{-1} respectively for foxed, not foxed and reduced areas. In the region 1700–1740 cm^{-1} we found the peaks of not conjugated keto groups ($R_1R_2C=O$) at 1710 and 1700 cm^{-1}, 1720 cm^{-1} and 1736 cm^{-1} respectively, for foxed, not foxed and reduced areas. Foxed and unreduced papers gave an intense peak while reduced papers gave only a weak shoulder due to an incomplete reduction of carbonyl groups. In spectra collected from only foxed areas (Fig. 1) a peak at 1960 cm^{-1} was present. This is the spectral region of the absorption of allenes (antisymmetric C=C=C stretching).

Sample 2

Spectra reveal the presence of carbon-carbon triple bonds with peaks at 2294 cm^{-1}, 2205 cm^{-1}, 2136 cm^{-1} for foxing stains; at 2234 cm^{-1} and 2135 for foxed-reduced areas. At 1741 cm^{-1} and 1800 cm^{-1} peaks are present that can be attributed to

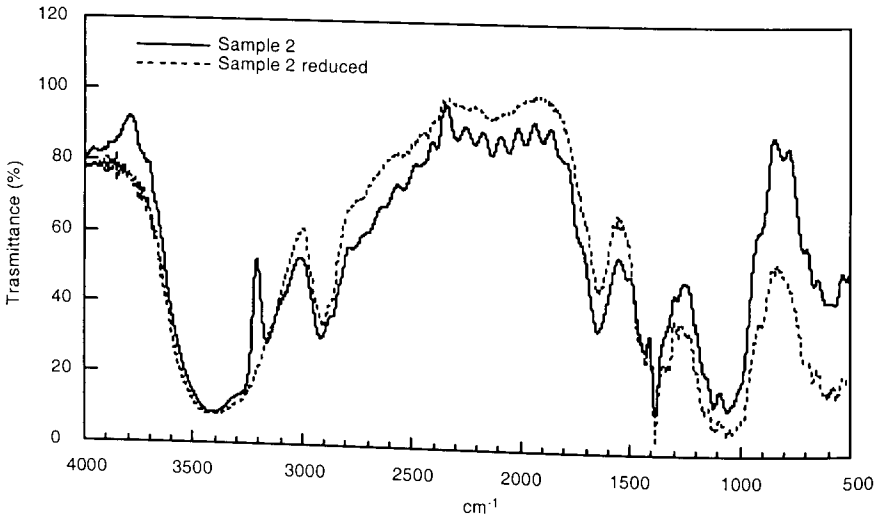

Figure 2: Infrared spectra of foxed areas in Sample 2 before and after reduction treatment.

lactones, esters, cyclic anhydrides or carboxylic acid salts; all these structures can be present in oxidized papers. After reduction these peaks disappear. Peaks arising in the regions 1360–1450 cm^{-1} and 1540–1650 cm^{-1} confirm the presence of carboxylic acid salt. Carbon-carbon double bonds (-C=C-) typical absorption, if present, are masked by the broad band of bonded water, centred at 1640 cm^{-1}.

An example of typical spectra collected on foxed and foxed-reduced areas is shown in Fig. 2.

Sample 3

The spectra are characterized for both kind of papers (foxed and not foxed) only by peaks related to triple bonds at 2246 cm^{-1} and 2127 cm^{-1} for foxed areas and at 2245 cm^{-1} and 2142 cm^{-1} for not foxed paper. As in sample 1, foxing (Fig. 3) is also characterized by a peak at 1995 cm^{-1} due to allenic structures, confirmed by the peak at 1061. In fact, allenes present C=C=C out of phase stretching in the region 2000–1900 cm^{-1} and in phase stretching in the region 1060–1095 cm^{-1}. A peak at 1736 cm^{-1} (C=O stretching) is also visible as a shoulder on the peak centred at 1638 cm^{-1}.

Sample 4

Only a foxed stain was analysed. The related spectrum is characterized by the peaks of carbon-carbon triple bonds (2347 cm^{-1}, 2328 cm^{-1}), not conjugated car-

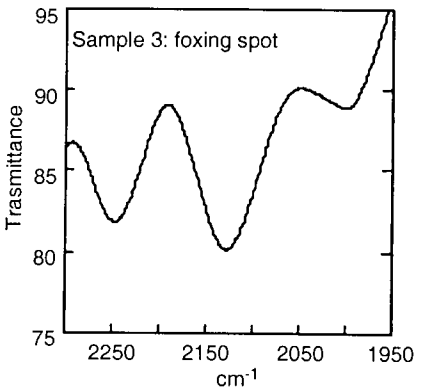

Figure 3: Sample 3, foxing spot, spectral region 2200-1950 cm^{-1}.

bonyl groups (1754–1715 cm^{-1}), double bonds on the ring (1656 cm^{-1}) and carboxylic acids salts (1540 cm^{-1} and 1356 cm^{-1}).

Sample 7, 8 and 9

No spectral differences were found between the three kinds of foxed spots. The spectra of the untreated papers show the presence of carboxylic acids salts, with peaks in the regions 1360–1450 cm^{-1} and 1540–1650 cm^{-1}, and not conjugated keto groups with peak at 1736 cm^{-1}. In both samples the foxed areas reveal the presence of carbon-carbon triple bonds with peaks at 2316 cm^{-1}, 2230 cm^{-1}, 2130 cm^{-1}. A peak at 2049 cm^{-1} could be attributed to ketene structures (pseudo-antisymmetric C=C=O stretching). Carbon-carbon double bonds (-C=C-) typical absorption, if present, are masked by the broad band of bonded water, centred at 1640 cm^{-1}.

XRF measurements

All the samples were analyzed with the X-ray microbeam spectrometer[15] of the LNS/INFN LANDIS laboratory (Catania)[16, 17].

XRF technique[18] is completely non destructive and it is sensitive to a great number of elements, typically those with atomic number $Z > 14$. Moreover, the 400 μm beam spot is particularly suited to analyzing stains the dimensions of which are usually in the order of 1 mm or less.

By pointing the beam at different points of the samples it was possible to compare the XRF spectra obtained from the foxing stains and those obtained from the "clean" paper.

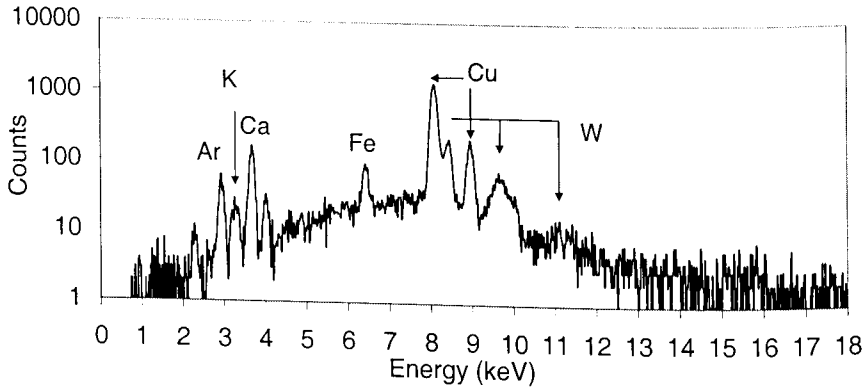

Figure 4: X-Ray spectrum obtained from not foxed paper in Sample1 The characteristic lines of tungsten (W) are due to the X-ray tube of the microbeam spectrometer, while the argon peak is due to the air presence.

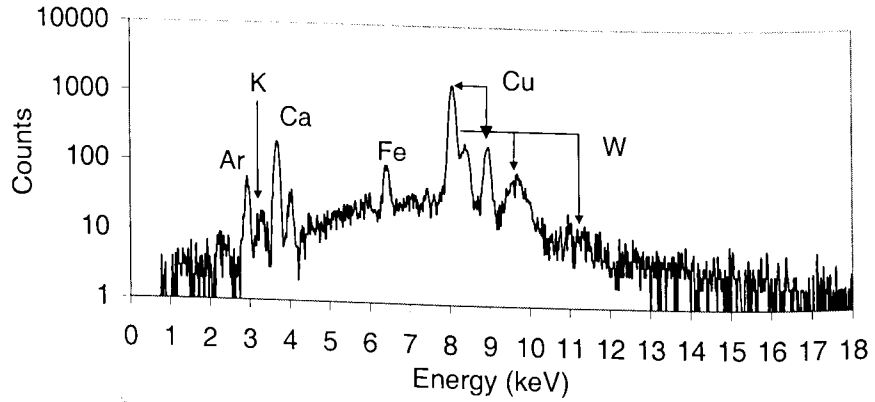

Figure 5: X-Ray spectrum obtained from a foxing stain in Sample1. The characteristic lines of tungsten (W) are due to the X-ray tube of the microbeam spectrometer, while the argon peak is due to the air presence.

The elements measured during the non-destructive analysis were Ca, Fe, Cu and K. It is important to observe that calcium is always present in the paper and it is not directly related to the foxing stains. In some cases iron and potassium were also detected on paper that was not foxed. The fluorescence counts of detected elements are reported for each analyzed sample. Data have been normalised to the argon peak (i.e. we report the ratio between the net area of each investigated element and the net area measured for the argon). The argon characteristic X-line in the spectra is due to the presence of air during the measurements. Its intensity depends on the experimental conditions and it is generally used to compare different measurements. The error on data is about 10%.

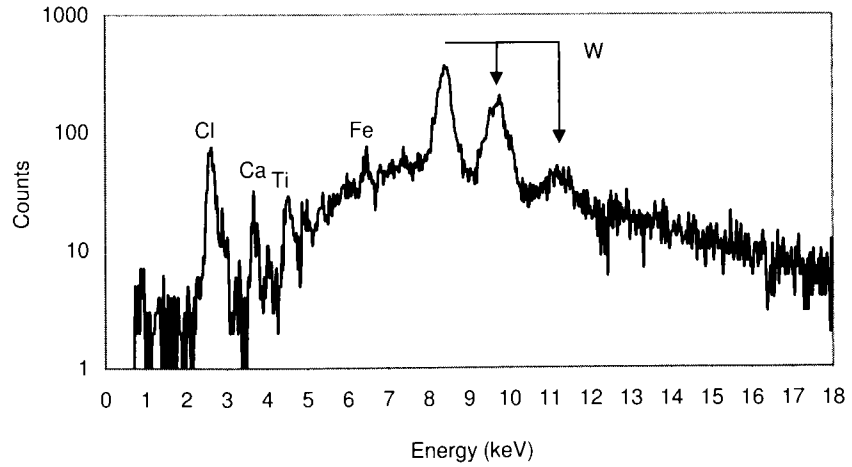

Figure 6: X-Ray spectrum obtained from a foxing stain in Sample 2. The presence of Cl, Ca, Ti and Fe is evident. The characteristic lines of tungsten (W) are due to the X-ray tube of the microbeam spectrometer.

Sample 1

XRF measurements show the presence of calcium, potassium, iron and copper both in foxing stains and in the clean paper (Fig. 4 and 5). The K/Ar, Fe/Ar and Cu/Ar ratio are reported on Table 8. Their values both for the foxing stains and for not foxed areas are similar. It is evident the presence of Cu and Fe both in the paper and in the different foxing stains. The potassium content is low. In this case the experimental data did not allow us to correlate the content of the detected elements with the foxing damage.

Samples 2 and 3

The X-ray spectra (Fig. 6) show the presence of iron, titanium, and calcium; in some points chlorine was detected. Data are reported in Table 8. The presence of iron is evident both in areas of the paper which were not foxed and in the different dark foxed stains. In sample 2 chlorine was detected in the fox marks. Titanium was probably an impurity in the paper. Analysis of data shows that there were no significant differences between the elemental composition of foxed and not foxed paper.

Sample 4

On sample 4 a systematic study of the paper surface was performed; both dark stains and light stains were analyzed. Experimental data are reported in Table 8.

Table 8: XRF data of samples 1– 6.

Sample	Description	Cl/Ar	Ti/Ar	K/Ar	Fe/Ar	Ca/Ar	Cu/Ar
1	paper			0.0	5.2		59.0
1	paper			0.4	1.5		33.8
1	paper			0.6	1.9		43.9
1	foxing			0.5	3.2		35.9
1	foxing			0.3	1.8		38.5
1	foxing			0.0	4.0		66.0
1	foxing			0.0	3.4		37.6
2	paper	0.0	1.4		3.2		
2	dark foxing	12.6	3.9		3.1		
2	light foxing	8.8	2.3		3.0		
3	paper	0.0	0.0		3.5		
3	dark foxing	0.0	0.3		3.7		
4	paper			0.1	1.5	2.2	
4	dark foxing			6.6	111.0	1.9	
4	dark foxing			9.9	114.2	1.8	
4	dark foxing			2.6	27.7	2.7	
4	dark foxing			2.3	54.1	2.7	
4	dark foxing			2.4	484.9	2.7	
4	dark foxing			2.3	62.8	2.8	
4	dark foxing			4.5	62.0	1.7	
4	dark foxing			3.3	39.3	2.3	
4	light foxing			0.3	2.4	2.1	
4	light foxing			0.5	2.0	2.6	
4	light foxing			0.6	2.0	2.9	
4	light foxing			0.5	2.3	2.2	
4	light foxing			0.4	2.0	2.9	
5	paper			0.0	1.3	2.8	
5	ink			0.0	1.3	2.6	
5	dark stain			2.4	73.4	3.1	
5	dark stain on ink			1.8	81.6	3.0	
6	paper				2.1	1.6	
6	dark stain				6.5	2.8	
6	dark stain				10.5	4.1	
6	light stain				0.8	1.1	
6	light stain				1.3	1.3	

The iron and potassium content in the brown stains was substantially greater than that found in the light stains. In both cases an increase is evident when compared to the paper in areas that were not foxed.

Table 9: XRF of samples 7–9.

sample	Description	Ca/Ar			Fe/Ar		
		1 µl	3 µl	5 µl	1 µl	3 µl	5 µl
7	paper	5.6			8.1		
7	$FeCl_3$		2.0	1.9	1.8	4.8	5.1	6.6
7	$FeCl_3$		1.5	1.7	1.2	6.2	5.5	5.2
7	$FeCl_3$			1.4	1.0		5.3	5.2
8	paper	1.0			3.0		
8	paper	1.6			4.8		
9	$FeCl_3$ + KCl		0.5	0.7	1.1	2.9	6.1	6.6
9	$FeCl_3$ + KCl			0.9	0.9		4.2	6.1
9	$FeCl_3$ + KCl			0.6			6.0	
9	KCl		1.5	1.4	0.7	2.2	2.3	1.6

Sample 5

Foxing stains on the paper surface and on the ink were analyzed. Data are reported in Table 8. The iron content was relatively low both in the paper and in the ink. Potassium was not present either in the paper or in the ink. An increase of iron and potassium is evident on the foxing stains.

Sample 6

Dark and light foxing stains were analyzed. The iron content present in the dark stains was greater than that in the light stains and in the clean paper (Table 8). Potassium was not present.

Samples 7, 8 and 9

Table 9 shows the results obtained from the measurements on the Umbria paper, treated with $FeCl_3$ and KCl solution.

These solutions (of 1, 3 and 5 µl) placed on the paper surface caused foxing stains the diameter of which was proportional to the applied volume of each solution. The area density was consequently about the same, even if the absolute quantities of the elements in the solutions were different. Table 9 reports the ratio between the net counts for Ca and Fe and those for Ar. The ratio Fe/Ar, measured with the X-ray microbeam spectrometer, was almost constant, except in some points. The variation of this ratio could be related to a different iron content at different points of the paper (iron in fact was also present in the "clean" paper) or to an inhomogeneous distribution of the applied solution. In this case we were not able to relate the formation of foxing stains to the iron content.

We want to emphasize that potassium was not detected during the measurements obtained by pointing the 400 μm beam directly on the foxing stains of sample 9. It has a mobility greater than iron. For this reason the iron remains localized in a region comparable to the beam dimensions while potassium is localized on the border of the stains, as reported in the previously described UV observations.

DISCUSSION AND CONCLUSIONS

IR and chemical analysis pointed out that the foxing phenomenon is related to a strong oxidation of the cellulose chain, as has been underlined by other researchers, with subsequent dehydration of the macromolecule. The oxidation can lead to carbon-carbon double or triple bonds, to carbonyls or carboxyls (both acid or esters), to lactonic, ketenic or allenic structures.

The presence of carbon-carbon double or triple bonds and conjugated systems of double bonds is indirectly confirmed also by L*a*b* chromaticity co-ordinates after reduction treatments: papers with a higher content of carbonyl groups in respect to other oxidized functions are more powerfully bleached after reduction, as for example Sample 1.

Examination under UV light showed that halos around the iron spots induced on Umbria paper (Samples 7 and 9) are fluorescent and not yet brownish. Probably, as for the case of iron gall ink[19], this halo could turn brown after further ageing that is scheduled in our laboratories.

XRF data analysis as well as UV observation show different results on different samples. In Samples 4, 5 and 6 a great concentration of iron and of potassium (the last in Samples 4 and 5) was found in the darker stains: transition[20, 21] and alkaline[22] metals can have a catalysing effect on oxidation reaction. This result does not appear in the other paper samples. We can argue that the only common characteristics for foxed areas is the oxidation of the cellulose macromolecule.

Probably the foxing phenomenon could be related to an intrinsic heterogeneity of the cellulose chains in the paper: greater or lower extensions and amounts of amorphous phases can induce different water content and the absorbing capability of pollutants and impurities introduced during the production of the paper; or which can be evenly present in the fibres. This could explain the presence of different zones with different oxidation capability.

In any case the problem of foxing needs further investigation.

The use of reducers can be helpful in contrasting foxing, especially when carbonyls and carbon-carbon double bonds are formed. Boron-based reducers also

seem to be effective to some extent on carboxyl, esters and lactones. This effect, too, needs further investigation.

SUMMARIES

Characterisation of foxing stains by chemical and spectrometric methods

Foxing stains on six different papers from the 16th–18th centuries and additionally fox-like stains produced by dripping different amounts (1, 3 and 5 μl) of solutions of $FeCl_3$, KCl and $FeCl_3$+KCl ($5 \cdot 10^{-3}$ M) on modern paper and artificially ageing were analyzed for chromaticity, fluorescence under UV illumination, carbonyl content, thickness and submitted to IR spectroscopy and XRF spectrometry. As a result it is stated that the foxing phenomenon is related to a strong oxidation of the cellulose chain. Not regarding certain and possibly specific differences between different kinds of foxing stains, this strong oxidation is the only common characteristics for foxed areas.

Caractérisation des taches de moisissure au moyen de méthodes chimiques et spectrométriques

Des analyses ont été faites sur des taches de moisissure de six différents papiers datant du 16ème au 18ème siècles ainsi que sur des taches ressemblantes sur du papier moderne, obtenues par addition de gouttes d'une solution de $FeCl_3$, KCl et $FeCl_3$ + KCl ($5 \cdot 10^{-3}$ M) en quantités différentes (1, 3 et 5 μl) et après vieillissement accéléré. Les analyses portaient sur la chromaticité, la fluorescence sous l'effet de la lumière UV, la teneur en carbonyle et l'épaisseur; ensuite ces taches ont été soumises à une spectroscopie IP et à une spectroscopie XRF. Le résultat observé démontre qu'il existe un rapport étroit entre l'apparition des taches de moisissure et une forte oxydation de la chaine cellulosique. Indépendamment du fait qu'il existe certaines différences et probablement des différences spécifiques à chacune des sortes de taches de moisissure, cette forte oxydation est la seule caractéristique commune à toutes.

Characterisation of foxing stains by chemical and spectrometric methods

Stockflecken auf sechs verschiedenen Papieren aus dem 16.–18 Jh. und zusätzlich entsprechend aussehende Flecken, die auf modernem Papier durch Auftropfen einer Lösung von $FeCl_3$, KCl und $FeCl_3$+KCl ($5 \cdot 10^{-3}$ M) in verschiedener Menge (1, 3 und 5 μl) und nachfolgender beschleunigte Alterung erzeugt worden waren, wurden auf Farbwerte, Fluoreszenz unter UV-Licht, Gehalt an Carbonylgruppen und Dicke untersucht sowie einer IR-spectroskopischen und einer XRF-spectrometrischen Untersuchung unterworfen. Als Ergebnis wird konstatiert, daß Stockflecken einhergehen mit einer deutlichen Oxidation der Cellulosekette. Unabhängig von gewissen und möglicherweise verschiedene Arten von Stockflecken charakterisierenden Unterschieden ist diese deutliche Oxidation das Einzige, was allen Stockflecken gemein ist.

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Study of the Photo-Oxidation of Mass-Deacidified Papers

by JAVIER DUFOUR & JOHN B. G. A. HAVERMANS

INTRODUCTION

Chemists have long been aware of the acidity phenomenon. As early as the mid-nineteenth century, studies by Faraday, as well as by Calvert and Letbaly, raised the alarm about the harmful effect of acidity on books[1]. Books dating from the 15th century show almost no deterioration, library authorities estimate that most of the books printed between 1850 and 1950 will not last out the present century, and those books printed between 1900 and 1937 have a useful life of only 50 years[2]. In this way, several treatments have been developed in the last decades in order to eliminate this acidity and to yield some alkaline reserve in the documents affected.

Water-based treatments are essentially confined to manual conservation treatment due to the solubility of certain pigments and adhesives used in books and to the necessity of long drying periods[3]. Gaseous processes have also been tested because of their easier diffusion inside the stacks of documents to be deacidified. The first gas used was ammonia mixed with water vapour, but the results obtained were not satisfactory[4]. Other attempts were based on the use of mixtures of morpholine and water vapor[5], ammonia and ethylene oxide[6] and a semi-gaseous process, the *Interleaf vapour phase deacidification*, using cyclohexylamine carbonate; these processes presented serious health hazards, even for the readers in some cases.

Besides several experimental deacidification plants, the most well known processes on a mass scale are the gaseous process DEZ and the organic solvent-based processes Battelle, Bookkeeper, FMC, WeiT'o and the Sablé variant of the latter. The principle of all these treatments is the neutralization of the acid compounds which are present in the paper, by reaction with the treatment chemicals. The corresponding hydroxide and carbonate are formed by hydrolysis and adsorption of CO_2 from the effective agents. Both the hydroxide and carbonate can react with the acids and build up an alkaline reserve. The processes mentioned are summarized as follows.

DEZ process

This process was developed since 1977[7] first by the US Library of Congress, then by AKZO Chemicals Inc. and closed down in 1993. Its name derived from the use of diethylzinc as the basic compound. The compound can react with acids, neutralizing them and with water or oxygen to produce the alkaline reserve. The ZnO and $ZnCO_3$ produced can react with new acids formed by the action of pollutants or by hydrolysis. The amphoteric nature of the ZnO compound allows the reactions with alkaline compounds, yielding zincates. The process includes three stages[8]:

- Predrying. The books are placed on carts separated by spacers. The autoclave used is purged with nitrogen and then a vacuum is produced. The books are kept at 40°C for more than 12 hours until a moisture content of 0.4% is reached. This moisture can be controlled to yield up to 3.5 % ZnO during the following stage. After drying, nitrogen is flushed into the system in order to make the environment inert.
- Permeation. DEZ is introduced into the chamber, the working pressure is 15 torr while the temperature increases from 21°C to 54°C. This stage takes approximately 12 hours. Excess DEZ is removed by purging with nitrogen and the temperature is decreased to 15°C.
- Reconditioning. Water vapour is flushed through at 54°C for 6 hours followed by a 3-day humidification.

Battelle process

The solvent used by the Battelle process (Battelle Ingenieurtechnik GmbH) is hexamethyl disiloxane (HMDO, $(CH_3)_3SiOSi(CH_3)_3$). It is a silicone, which are expected to have an inert behaviour in relation to paper. Magnesium titanium ethoxide (METE) was selected as the basic agent because this compound is totally soluble in the HMDO[9]. A surfactant is added to improve the impregnation. The ethoxide yields Mg and Ti hydroxides by hydrolysis. The magnesium hydroxide reacts with the acid compounds of the paper or with CO_2 producing the carbonate. The titanium hydroxide is converted to inert titanium oxide (TiO_2) through several reactions. The magnesium carbonate and the residual metal hydroxides neutralize the acids and form an alkaline reserve. The process can be divided into four stages:

- Pre-drying. The paper is dried for 2 days in a vacuum at 60°C to achieve a moisture content of between 0.5 and 1%.

- Impregnation. The solution is kept in contact with the paper documents for few minutes and the excess of the solution is drained out.
- After-drying. This stage is carried out as in the pre-drying step.
- Reconditioning. After drying, the documents are reconditioned for 3 weeks in a well-ventilated storage room to restore the normal water content and diminishing the characteristic odour of ethanol produced during the treatment[10].

Bookkeeper process

The Bookkeeper process (Preservation Technologies Inc.) uses MgO particles as the basic agent suspended in the organic solvent perfluoro heptane. The process was modified in 1995 in such a way that a lower concentration of MgO and smaller particles are used as well as a surfactant, which was introduced for improving impregnation. The magnesium oxide particles rapidly absorb water and form magnesium hydroxide, which reacts with the acid compounds. The process consists of:

- Pretreatment. The paper documents are dried in a vacuum.
- Impregnation. After the pressure is equalized, the deacidification suspension is introduced and the documents are agitated for 15–20 minutes. The suspension is drained out.
- Aftertreatment. The documents are dried for 90 minutes in a vacuum.
- Reconditioning. The documents and books are stored in an open room for 24 hours in order to reestablish the water content.

FMC process

This process was developed by the Lithium Division of the FMC Corporation. It was based on the use of magnesium butoxytriglycolate (MG-3) dissolved in freon-113. In the last few years several changes have been made in the treatment solution: MG-3 has been replaced by magnesium butyl glycolate (MBG) and the freon by heptane [3,11]. The effective agent reacts directly with the acid compounds of the paper and a carbonate is formed as well by the CO_2 being liberated by the hydrolysis of MG-3. The remainder of the MG-3 and the carbonate produced establish the alkaline reserve. The steps of the procedure are:

- Pre-drying. A dielectric process is used to achieve a moisture content of 2%.
- Impregnation. This step takes between 5 and 10 minutes.

- After-drying. The remainder of the solvent in the books and documents is removed using the dielectric process.

WeiT'o and Sablé processes

The deacidifying solution of the WeiT'o process (WeiT'o Associates Inc.) was initially magnesium methoxide in methanol and freon-12, which were supplemented with barium methoxide and freon-11 and freon-113 when separate sheets were treated. In order to improve the method, the basic compound was changed to methyl methoxy magnesium carbonate (MMMC), freon-12 was replaced, in a first step, by freon-122, a more environmentally-friendly compound, and now by hydrochloro-fluoro carbons. Also, the methanol content was decreased due to its damaging effects on certain inks[3].

The Sablé method, as developed by the Centre de Recherche sur la Conservation des Documents Graphiques and CIM-Mallet, is derived from the WeiT'o technique. The basic compound is a mixture of methyl methoxy magnesium carbonate (MMMC) and methyl ethoxide magnesium carbonate (MEMC). The initial solvent of freon-12 and methanol was changed to freon-134a and ethanol[1,12]. The MMMC or MEMC produce $Mg(OH)_2$ by hydrolysis and this reacts with carbon dioxide yielding magnesium carbonate. The process is carried out in the following steps:

- Selection. Due to the harmful effect of alcohol, books and documents with certain inks and adhesives have to be excluded.
- Pre-drying. This step takes between 36 and 48 hours at 60°C and then a vacuum is created until a moisture content of 0.5% is reached.
- Impregnation. A vacuum is created and the treatment solution is introduced under pressure. The contact time is between 10 and 60 minutes and then the solution is pumped out.
- After-drying. The books and documents are dried for 60 minutes in a vacuum.
- Reconditioning. 12–48 hours in room conditions.

Many studies on the effects of thermal treatment and air pollutants on the aging of deacidified papers have been conducted. However, studies dealing with photo-aging are found very rarely. Researchers conducting such studies often state that Zn and Mg-compounds can enhance the yellowing of paper.

The aim of this research is not to compare the efficiency and success of the previous cited processes. As is shown in the following sections, the photo-degradation process used produce a rapid oxidation by using pure oxygen and

high temperature under illumination. Therefore, it can differ from actual aging of untreated or treated papers. The objective of this paper is to contribute to the understanding of the degradation pathways of deacidified papers, comparing the effect of Mg and Zn.

Materials and Method

Most paper and cellulose-based documents are usually exposed to visible and UV-A spectra during their normal use, as window glass filters most UV-B radiation in sunlight. Therefore, the light spectrum selected for this study is in the 300–600 nm region with a peak at 365 nm. In this way, the photo-degradation of wood-free papers occurs through the photochemical initiation of free radicals without the chemical changes proposed by Philips et al.[13] or by photo-sensitization from the presence of impurities, such as hemicelluloses, or external compounds, such as fillers[14]. On the other hand, groundwood-containing papers are photo-degraded by photo-sensitization promoted by a high lignin content[15,16]. In both cases oxygen plays a basic role either by adding to conjugate systems in photo-sensitized degradation or by reacting in propagation of radicals (reactions (1) and (2)). Therefore, it is possible to study the photo-degradation of paper by following its oxygen consumption.

$$RH_2C\cdot + O_2 \rightarrow RH_2C\text{–}O_2\cdot \quad (1)$$

$$RH_2C\text{–}O_2\cdot + RH_2C\text{–}H \rightarrow RH_2C\text{–}OOH + RH_2C\cdot \quad (2)$$

Testing equipment

The testing equipment (Fig. 1) is based on this fact. This system continuously measures oxygen uptake during irradiation of the paper sample. It is further based on the assumption that essentially all pressure changes are due to the consumption of O_2. Therefore, all other major volatile photo-oxidation products, mainly CO_2 and H_2O, are adsorbed into 5A type molecular sieves, which are added to the closed gas system. In order to accelerate photo-degradation, pure oxygen was chosen. The sample is placed on the outer wall of the cooling tube in front of the light source. The lamp and cooling tube plus sample are placed in a double-walled reaction vessel. The gas in this vessel can be kept at a pre-set temperature with the aid of circulating water from a thermostat. In our research, a temperature of 70°C was selected in order to accelerate the reactions, because the irradiation in the near ultraviolet makes the rate of yellowing of irradiated samples

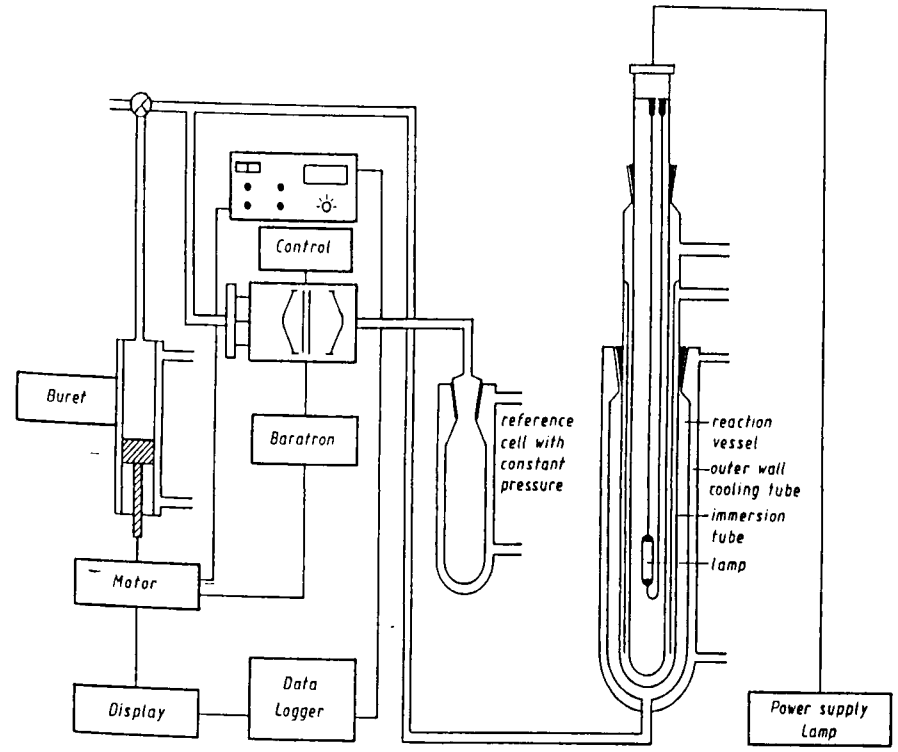


Fig. 1: Testing equipment.

more sensitive to increased temperature[17,18] and higher temperatures promote the thermal degradation.

The vessel is in direct contact with a gas burette, while a differential manometer (Baratron) is located between the reaction vessel and a reference cell. The reference cell contains a constant volume of gas at a constant temperature and it is, therefore, at constant pressure. O_2 consumption by the paper causes a pressure difference between the two vessels, which is detected by the baratron. This pressure difference is compensated by a displacement of the piston in the burette, which is controlled by the baratron. The displacement of the piston is registered by a potentiometer.

Paper sample

There appears to be a general consensus on the type of paper that benefits most from deacidification: paper which is acidic, such as alum-rosin-sized and ground-

Table 1: Conditions of mass-deacidifcation treatment of the testing material.

Process	Date of treatment	Basic agent	Solvent	Additives
Battelle	June 1994	METE	HMDO	Surfactant
Bookkeeper1	Nov. 1994	MgO	Perfluoro heptane	–
Bookkeeper2	July 1996	MgO, smaller particles	Perfluoro heptane	Surfactant
DEZ	Feb. 1994	DEZ	–	–
FMC	Nov. 1992	MG-3	Freon-113	–
Sablé	Mar. 1993	MMMC + MEMC	Ethanol + Freon-12	–

wood-containing paper, paper produced under acidic conditions and paper of all types which has become acidic by pollution[3]. In this way an acid, mechanical pulp paper was selected as a testing material. It was previously used in an EC research project[1]. Its fiber composition is 75% groundwood and 25% sulfite bleached softwood cellulose. Hemicelluloses were also present. It contains 20% of kaolin as a filler and is alum-rosin sized. Separated sheets of this paper were mass-deacidified by DEZ, Battelle, Bookkeeper, FMC and Sablé processes. Table 1 summarizes dates and chraracteristics of the processing.

The morphology of the samples was studied by SEM (Scanning Electron Microscopy) and the composition changes by FTIR (Fourier Transform Infrared Spectroscopy). The transmission spectroscopy in KBr was carried out on paper samples, using a Biorad FTS 60A FTIR apparatus with a triglycine sulfate, TGS, pyroelectric detector. Spectra were obtained in a range of 4000 – 400 cm^{-1} (25 μm to 2.5 μm) with a resolution of 2 cm^{-1}. The samples were obtained by scraping with a lancet about 1 mg of paper from the sheet and mixing this sample with about 300 mg KBr (Merck, spectroscopic grade). The subsequent mixture was transferred to a die and pressed to a KBr pellet using a pressure of 8 to 10 tonnes for 10 minutes. All transmission measurements were carried out at least in duplicate. The spectra obtained were base line corrected by setting the intensities at the points 4000, 2600, 1900, 840 and 400 cm^{-1} to 0.

Four indexes were calculated in order to estimate the effect of the oxidation. An index is the calculated value after the treatment, divided by the reference, i.e., the value of the untreated material:

- **CI**. The change in the morphological structure of the cellulose present in the two domains of the paper was calculated from the intensities of the bonds obtained at 1372 cm^{-1} and 2900 cm^{-1}. This is referred to as the crystallinity index (CI) of the cellulose. Where CI=absorption of the bonds at 1372 cm^{-1}/2900 cm^{-1}.

- **COI**. The effect of the oxidation was calculated by two indexes. Firstly, the index calculated from the carboxyl groups formed after the oxidation, i.e., calculated from the intensities of the bonds obtained at 1740 cm^{-1} and 2900 cm^{-1}. This is the COI (carboxyl index)= absorption of the bonds at 1740 cm^{-1}/2900 cm^{-1}.
- **OxI**. The second index to calculate oxidation was the effect of oxidation related to the glycosidic bond in the cellulose molecule and the degree of oxidation in the cellulose ring structure as calculated from the intensities of the bonds obtained at approximately 1160 cm^{-1} and 1372 cm^{-1} corresponding to the (hemi-acetal C-O-C) and the C-H bond. This is the OxI (oxidation index) = absorption of the bonds at 1160 cm^{-1}/1372 cm^{-1}. If oxidation took place at the C2 or C3 position, OxI will increase, while oxidation at the glycosidic bond will lead to a reduction of the amount of glycosidic bonds, e.g., depolymerization of the fiber and resulting in a decreasing value of OxI.
- **LI**. Finally the lignin index, LI, was calculated from the intensities of the bonds obtained at 1510 cm^{-1} and 2900 cm^{-1}. The aromatic index shows the relative degradation of the lignin present in the mechanical pulp sample due to oxidation.

As well as infrared analysis, the folding number in the machine direction (MD), ISO R-457 brightness and yellowing were also determined.

RESULTS AND DISCUSSION

Mass-deacidification treatment

The deacidified papers were characterized again (Table 2) for the development of this work (June–December 1996) and no significant differences were found with respect to the analysis carried out just after the deacidification treatments[1,9], i. e., no aging effects were detected. Fig. 2 and 3 summarize the results and Fig. 5 shows the micrographs of the deacidified papers. In this paper, the term "standard" is used for the groundwood-containing paper without mass-deacidification treatment.

All the deacidification treatments provoke certain degradation in the samples as the CI shows. According to the literature, this degradation could be expected, caused by the cleavage of the ß-glycosidic bond (alkaline hydrolysis) or by peeling[19, 20], but a third mechanism is also occurring, oxidation (or degradation) of the hydroxyl groups at the positions C2, C3 in the cellulose ring. The former should be more important than oxidation, but the increase in the OxI's demonstrates

Table 2: Several qualities before and after deacidification treatments.

	FTIR-indexes CI	COI	OxI	LI	Folding number MD	R-457 brightness	R-457 yellowing	Mg deposit (g/kg paper)
untreated	1	1	1	1	770±241	58.90±0.56	17.81±0.42	
Battelle	0.93	0.87	1.02	0.91	419±277	55.50±0.89	19.64±0.37	4.1 – 5.0*
Bookkeeper1	0.93	0.93	0.98	0.88	681±196	59.67±0.48	20.38±0.36	3.0 – 4.0
Bookkeeper2	0.85	0.93	0.93	0.9	732±173	60.96±0.36	15.96±0.08	1.5 – 2.0**
DEZ	0.87	0.83	0.97	0.94	627±233	56.69±0.08	16.88±0.11	
FMC	0.83	0.53	1.13	0.78	256±117	55.50±0.89	21.96±0.39	2.2 – 11.0***
Sablé	0.83	0.92	0.93	0.97	636±237	58.60±0.40	16.96±0.52	0.7 – 2.7

* plus 8–10 g Ti

** The concentration of Bookkeeper2 is estimated to 50% as compared to Bookkeeper1; therefore, the deposition as also been estimated to 50%.

*** A considerable variation with respect to position was observed. The highest value was measured at the top edge of the sheets. Average value: 4.5 g

that the FMC and Battelle processes degrade the samples mainly in the cellulose ring by oxidation, especially the FMC treatment, while the rest of the processes go through alkaline hydrolysis.

As expected, since this is the aim of these processes, the COI is decreased by all the treatments, because the basic agents neutralize the acid compounds present in the samples and the acid groups formed due to the degradation produced by the same deacidification treatment. The FMC is the heaviest treatment, producing a decrease of the carbonyl and carboxyl index of almost 50%. The rest of the processes reduce the COI less and their results are comparable. Degradation of the lignin was found as well, since the LI and, therefore, the aromaticity were decreased. The FMC process substantially decreases the LI up to 20%, suggesting that the paper structure is seriously modified.

All these paper modifications are observed in the MD folding number as well. The FMC and Battelle samples show values much lower than those papers deacidified by the other methods. This fact suggests that, for our acid-mechanical pulp, cellulosic ring degradation produces a higher decrease in the mechanical property than the cleavage of glycosidic bonds. In this way, the FMC process produces a dramatic decrease of the folding number down to values similar to those of photo-degraded papers. This phenomenon can be observed in the micrograph of the sample treated by this process (Fig. 5). The fibers of the FMC treated paper show a comparable deterioration to those of photo-treated samples. A lot of fines and many fracture lines can be seen on the fibers.

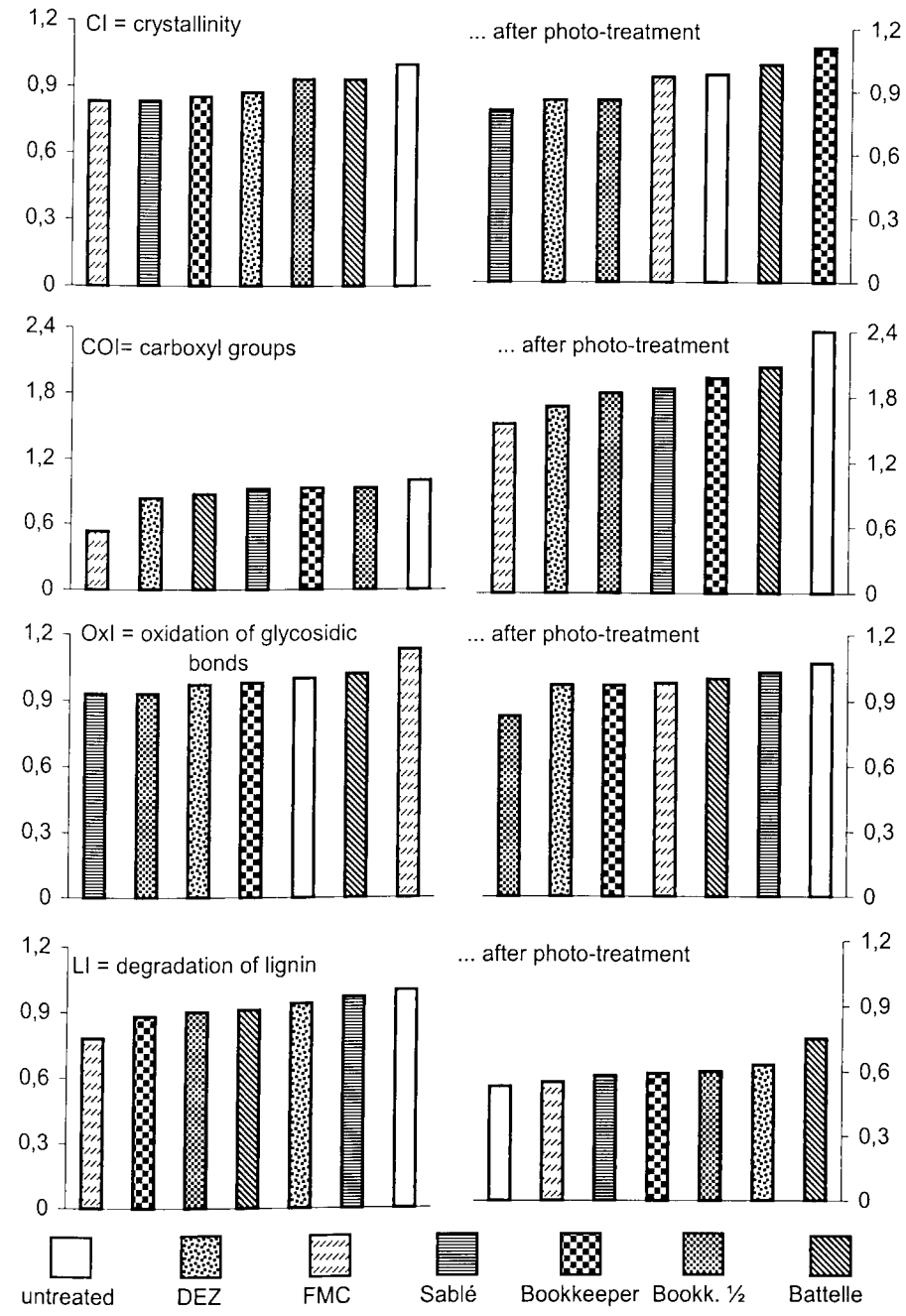


Fig. 2: FTIR indexes; of mass-deacidified samples, before and after photo-treatment

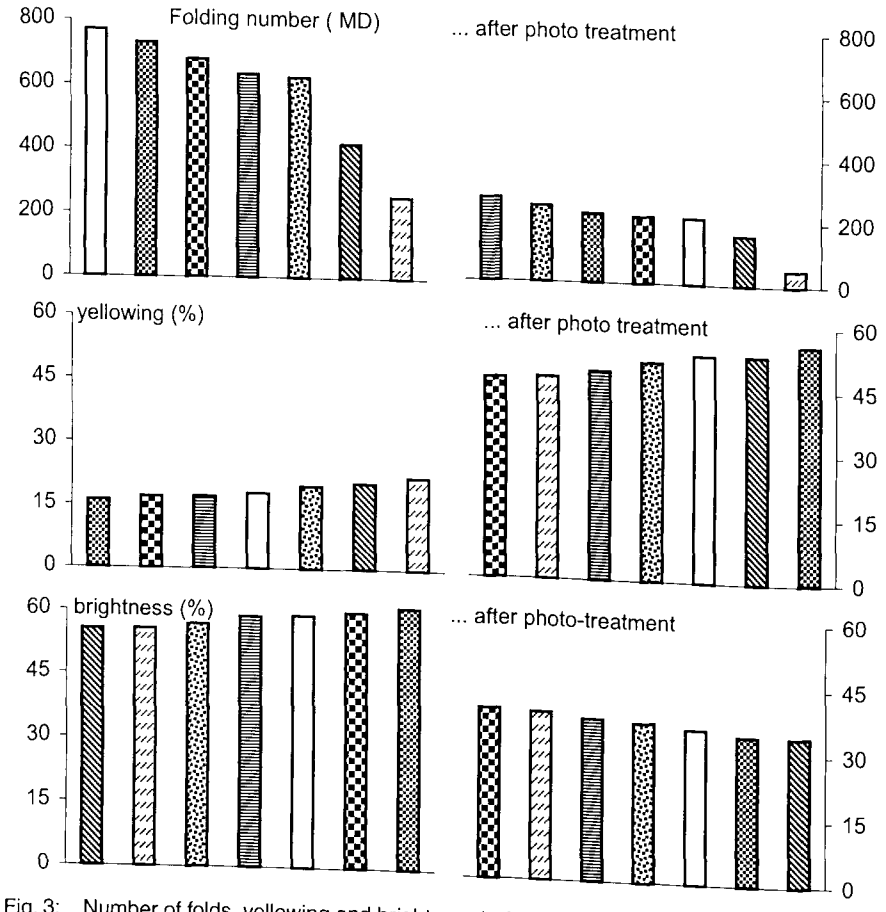


Fig. 3: Number of folds, yellowing and brightness before and after photo-treatment

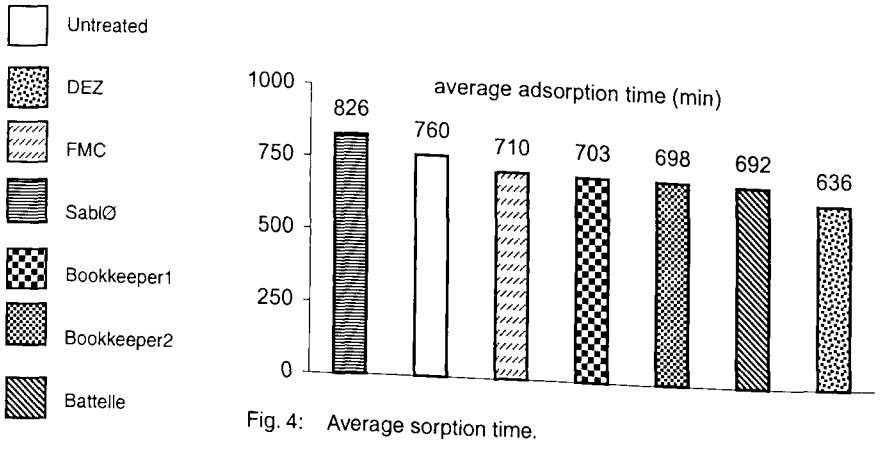
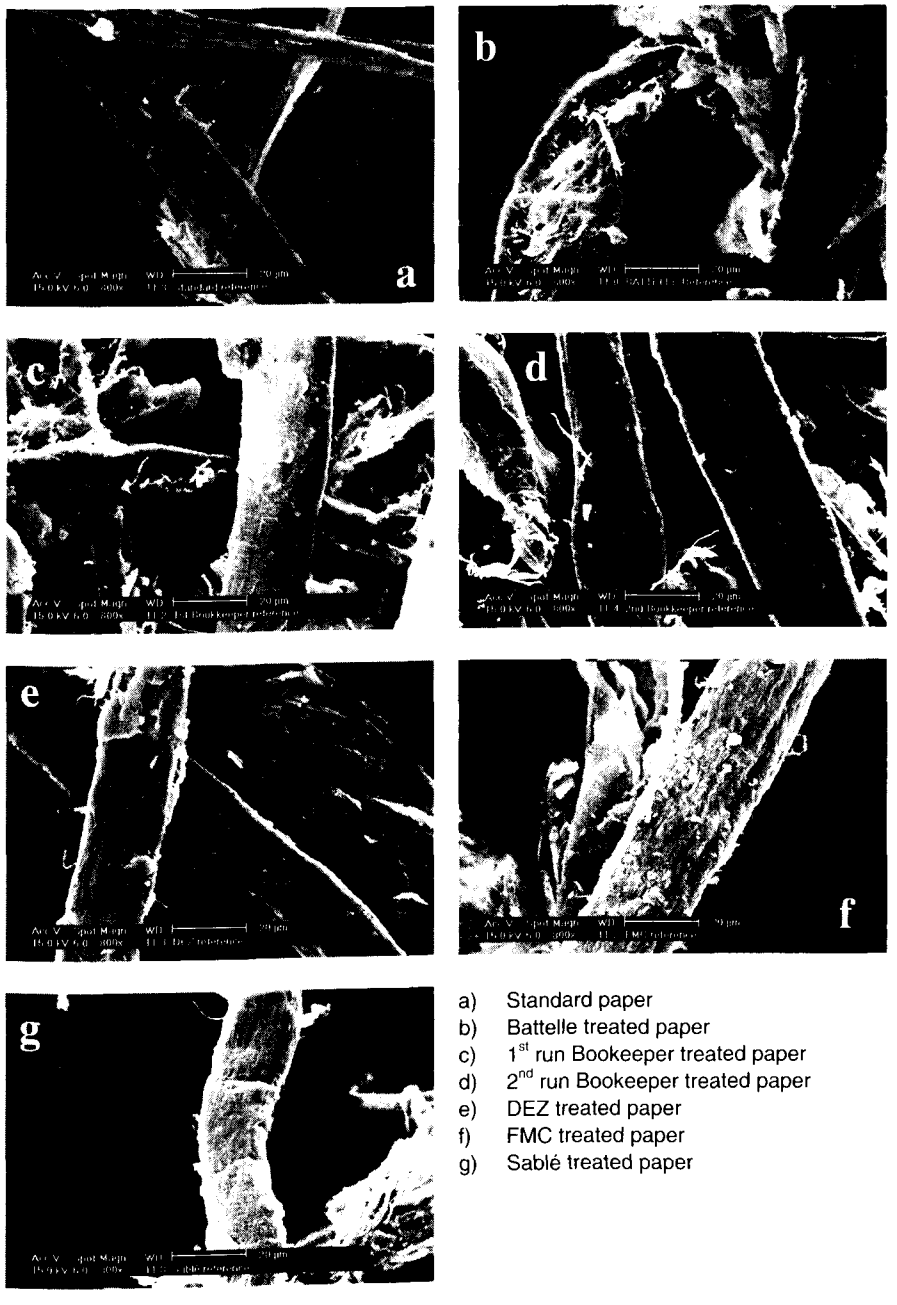


Fig. 4: Average sorption time.



a) Standard paper
b) Battelle treated paper
c) 1st run Bookeeper treated paper
d) 2nd run Bookeeper treated paper
e) DEZ treated paper
f) FMC treated paper
g) Sablé treated paper

Fig. 5: Micrographs of mass-deacidified papers.

The Battelle process shows a negative effect on the folding number as well, but the decrease is smaller than for FMC, probably due to less degradation in the ring and to less degradation of the lignin.

The DEZ, Sablé, Bookkeeper 1 and 2 decrease the folding number MD as well, but to a lesser extent, because these treatments act by cleaving the glycosidic bond. The condition of the fibers is comparable for all these treatments.

If we study the Mg deposition of each process (cf. Table 2), there appears to be a direct relation between these deposition rates and the folding number, and, therefore, with OxI. The Mg deposition rates were measured in previous works[1,9], depending on the kind of alumsized paper and the location on the sheet.

The highest Mg-deposition corresponds to the highest OxI and the most degraded papers. This probably means that the basic agents degrade first, the glycosidic bonds by alkaline hydrolysis, but when an overdeposition is produced, the excess of basic agent reacts at C2, C3 positions in the cellulose rings, beginning with the groups in the amorphous part and continuing with those groups in the crystalline part. This attack to the crystalline part produces a greater degradation and a decrease in the CI. This fact implies a serious consequence. An excess of the basic agent, which was considered to have no effect on the paper and to contribute to a build up of a higher alkaline reserve, can seriously degrade the treated papers. We must bear in mind that not only the deposited amount is important, but also the nature of the basic agent and the kind of neutralizing reactions are important.

This fact also explains the differences found between both runs of the bookkeeper process. The second process has a lower OxI, because the Mg-deposition is 50% less than with the first run. The differences of this second run from Sablé, with a similar Mg-deposition, could be due to the different degree of swelling produced by the inclusion of the basic agent in the fiber structure of the paper or by the drying out and reconditioning of the samples during the treatments.

The OxI of the DEZ samples is close to 1, suggesting that degradation is occurring by both mechanisms at a similar rate, but with a slight trend to depolymerization by cleavage of the ß-glycosidic bond.

As expected, the ISO-brightness and yellowness R457 are related and the most degraded papers show the greatest yellowing. The yellowing is also related to the COI: the lower the COI, the greater the yellowing. This is true for FMC, Battelle and DEZ the COI indexes of which are below 0.9. The other tested materials (with COI indexes higher than 0.9) are less yellow than the standard. This is probably due to the dark neutralization products formed after the deacidification treatments. The brightness shows the contrary, i. e., the lower the COI, the lower the brightness. The processes which yield a COI higher than 0.9 show a very similar brightness to the standard (Sablé) or a higher value (Bookkeeper1 and Bookkeeper2). This slightly higher brightness can be attributed to the use of an inorganic compound (MgO) as the basic agent.

Table 3: The measured qualities (cf. Table 2) after photo-treatment.

	FTIR-indexes				Folding number	R-457	R-457
	CI	COI	OxI	LI	MD	brightness	yellowing
Untreated	0.98	2.4	1.07	0.53	211±81	35.64±2.34	53.24±3.48
Battelle	1.03	2.07	1.00	0.75	159±101	34.18±0.73	53.35±0.49
Bookkeeper1	1.11	1.97	0.97	0.59	213±71	39.12±1.33	47.10±1.24
Bookkeeper2	0.86	1.83	0.83	0.60	220±153	34.34±0.79	55.77±1.27
DEZ	0.86	1.71	0.97	0.63	243±77	36.79±0.77	51.32±2.28
FMC	0.97	1.55	0.98	0.55	51±24	38.64±1.16	47.47±1.56
Sablé	0.81	1.87	1.03	0.58	265±129	37.40±0.50	49.06±1.36

Photo-treatment

Fig. 6 shows the experimental oxygen consumption curves obtained for each tested material and Fig. 7 shows the average curves estimated from the previous experimental data. The oxygen adsorption is expressed as a fraction of the total adsorbed O_2 volume (5 ml) vs. time. Fig. 4 summarizes the average adsorption time, Table 3, Fig. 2 and 3 the FTIR indexes, the MD folding number, the ISO-yellowing and the ISO-brightness R457 of the photo-treated samples, respectively.

The standard paper photo-degrades according to the photo-sensitized mechanism proposed in the literature[14–16] where the lignin acts as a photo-sensitizer. These previous works showed that the presence of lignin promotes the formation of free radicals and chemical oxidation. The yellowing of lignin-containing pulps was attributed to the formation of keto, aldehyde and carboxylic groups. The radicals formed on the cellulose backbone were hydrogen atoms and formyl radicals and hydroxyl groups on the surface. Carbonyl and carboxyl groups were considered as responsible for the initiation of the process[21, 22]. The hydroxyl groups react to yield carbonyl groups and hydrogen. Once formed, the carbonyl groups provide an autocatalytic influence[21]. Our experimental results (Table 3, Fig. 2) confirm that this is the most important mechanism because the OxI demonstrates that oxidation has taken place at the C2, C3 positions in the cellulose rings and the COI is largely increased due to the formation of carbonyl and carboxyl groups as well as to the degradation of the lignin. Nevertheless, the

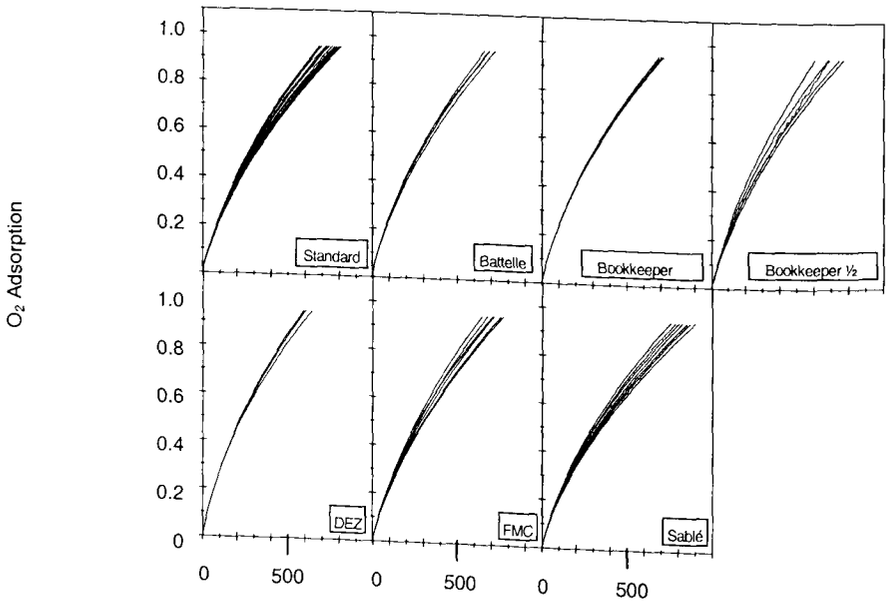


Fig. 6: Experimental photo-oxidation curves.

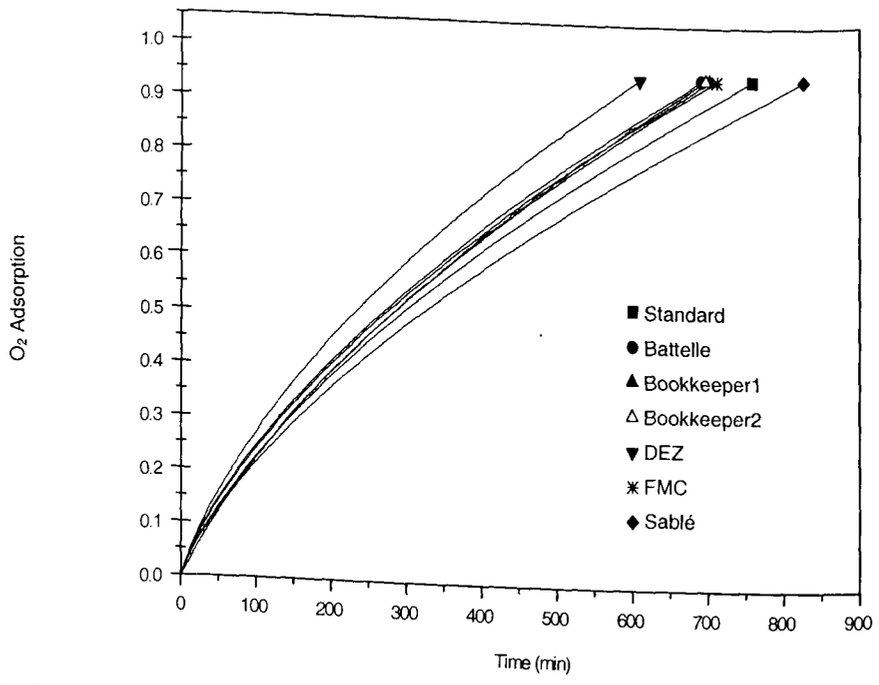


Fig. 7: Average photo-oxidation curves.

samples also degrade by depolymerization because of the cleavage of the ß-glycosidic bond as a secondary process. It is important to notice that the results obtained could be affected if different amounts of lignin were in the sample.

If the photo-oxidation acts firstly on the hydroxyl groups on the surface, i.e., the amorphous part, and then on the same groups in the crystalline part, which are less accessible, a slowing down in the oxygen uptake could be expected after the deacidification treatment because less positions for the easy adsorption of oxygen will be available due to their degradation by the basic agent. This does not occur, except for the Sablé process. We can see (Table 1 and 2, Fig. 2) that for the Battelle process and the 1st run of Bookkeeper the OxIs are constant after the photo-treatment (1.02–1.00 and 0.98–0.97 resp.), while the FMC process and the 2nd run of Bookkeeper show a relative decrease during photo-treatment (1.13–0.98, 0.93–0.83), indicating that cleavage of the ß-glycosidic bond is occurring at the same rate as the oxidation in the ring or that the cleavage is the main degradation mechanism.

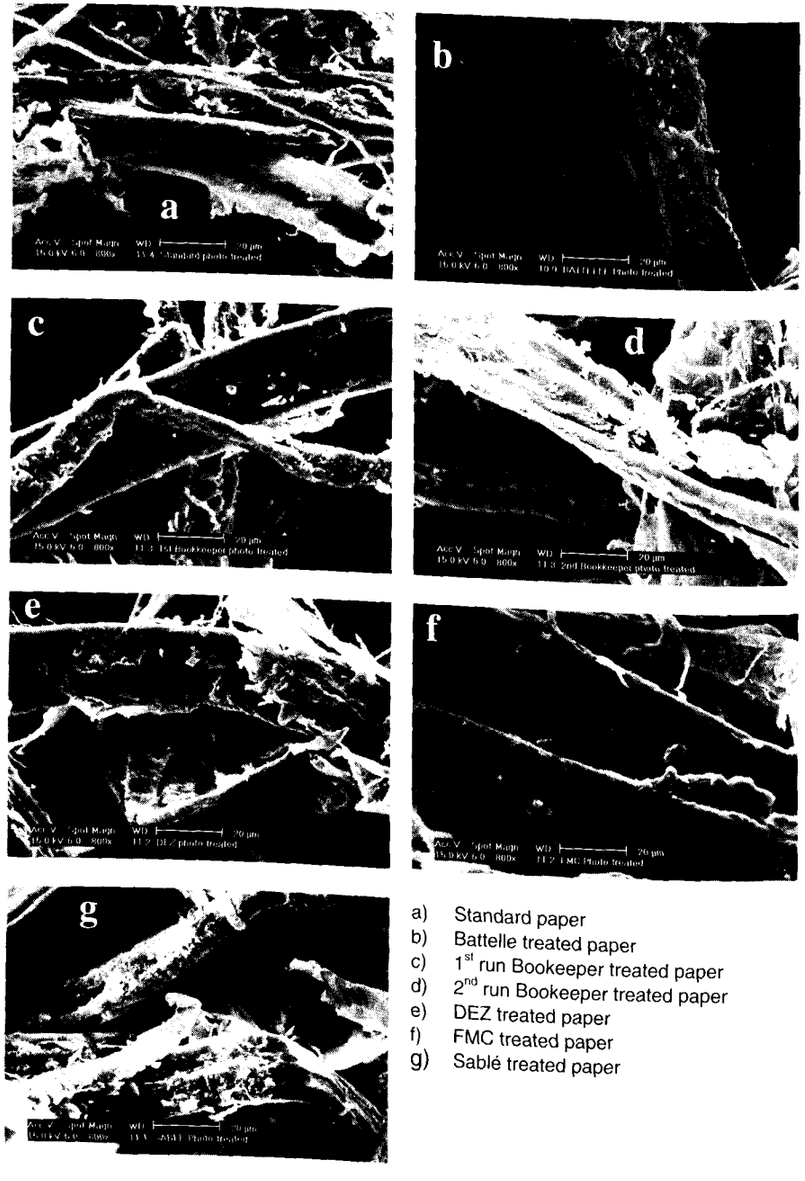
Only the samples treated by Sablé show a relative increase of the OxI (0.93–1.03: 11%), meaning that this is the only process which does not change the degradation mechanism. The explanation of this different behaviour could be due to the much lower amount of magnesium deposited in the samples, which is not enough to affect to the sample. Also the photo-degradation takes place on the hydroxyl groups at the C2, C3 positions in the crystalline part (less accessible), which requires longer adsorption times.

Based on these data, magnesium seems to exert a photo-sensitization effect, which is different from that promoted by lignin. Magnesium compounds accelerate the depolymerization mechanism by the cleavage of the ß-glycosidic bond, while lignin increases oxygen adsorption by oxidation in the cellulose ring.

The OxI of DEZ remains constant, indicating that both mechanisms of photo-degradation are occurring at similar rates. This suggests that the Zn compound is also increasing the relative speed of the cleavage of glycosidic bonds compared to the oxidation in the cellulose ring. This effect of accelerating the photo-oxidation is well-known[23, 24].

The COIs show a lower increment for the deacidified papers than for standard paper due to the previous degradation of the hydroxyl groups or to a different oxidation mechanism, which yields less carbonyl and carboxyl groups. The exceptions are the FMC and Battelle samples, but they are heavily degraded before the photo-treatment and, therefore, the estimated values are greatly affected by this error.

The final folding numbers of each sample summarize these observations. The values of FMC and Battelle are somewhat lower, but the values for the rest of samples are comparable to each other and to the photo-treated standard. This



a) Standard paper
b) Battelle treated paper
c) 1st run Bookeeper treated paper
d) 2nd run Bookeeper treated paper
e) DEZ treated paper
f) FMC treated paper
g) Sablé treated paper

Fig. 8: Micrographs of photo-treated papers.

means that for an oxygen adsorption of 5 ml, the degradation achieved is very similar for both mechanisms. This effect can be observed in Fig. 8 where the micrographs of photo-treated samples are shown. The most degraded samples exhibit a higher amount of fines and fracture lines.

Only the processes which use a surfactant yield higher yellowing and lower brightness than standard, suggesting that these additives enhance the photo-yellowing. The other processes produce better values than standard, but we must bear in mind that the adsorption times are quite short, except for Sablé.

CONCLUSIONS

In the conditions used for this research, i.e. rapid oxidation by pure oxygen at high temperature and intense illumination, the excess of a basic agent deposited on the paper during mass-deacidification processes, which build up the alkaline reserve, can greatly degrade the treated papers. Degradation is produced in the following way: the alkaline compounds degrade the β-glycosidic bonds by alkaline hydrolysis first and the excess material then also reacts at the C2, C3 positions in the cellulose rings, beginning with the groups in the amorphous part and continuing with the same groups in the crystalline part.

When the deacidified papers are photo-degraded, the presence of the basic agent promotes the degradation by cleavage of the β-glycosidic bonds, instead of oxidation at C2, C3 in the cellulose ring, which is the mechanism in the absence of alkaline compounds.

ACKNOWLEDGEMENT

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SUMMARIES

Study of the Photo-Oxidation of Mass-Deacidified Papers

The photo-oxidation sensitivity of deacidified papers was studied using previously developed testing equipment based on the measurement of oxygen consumption by the paper sample. Sam-

ples deacidified by five processes were evaluated: Battelle, Bookkeeper, DEZ, FMC and Sablé. The aim was to study the degradation mechanisms, analyzing the effect of the Mg and Zn deposited over the samples on the photo-degradation mechanism. To accelerate the process, pure oxygen, high temperature and intense illumination were used. By means of infrared, mechanical and physical analysis, it was suggested that the presence of basic compounds enhances the photo-yellowing. Cellulosic ring oxidation and the cleavage of the glycosidic bond were observed.

Analyse de l'oxydation induite par la lumière sur des papiers désacidifiés

L'étude de la sensibilité des papiers désacidifiés à la photo-oxydation a été réalisée au moyen d'instruments développés préalablement qui permettaient de mesurer la quantité d'oxygène consommée par l'échantillon de papier. Les mesures ont été faites sur des échantillons désacidifiés selon cinq procédés différents : Battelle, Bookkeeper, DEZ, FMC et Sablé. L'objectif poursuivi consistait à étudier les mécanismes de dégradation en analysant l'effet du Mg et du Zn déposés sur les échantillons au cours du mécanisme de photodégradation. Afin d'accélérer ce processus l'expérience a été effectuée en utilisant de l'oxygène pur, dans des conditions de température élevée et sous un éclairage intense. A l'aide de l'analyse infrarouge ainsi que de procédés d'analyse mécaniques et physiques il a été démontré que la présence de certaines substances renforçait le jaunissement induit par la lumière. Ont été également observées la cassure des composés cellulosiques par oxydation ainsi que la rupture de la chaine macromoléculaire glycosique.

Untersuchung zur lichtinduziertren Oxidation von massenneutralsiiertren Papieren

Es wurde die Empfindlichkeit von massenneutralisierten Papieren gegenüber der lichtinduzierten Oxidation untersucht. Hierzu diente eine vorher entwickelte Apparatur, mit welcher der Sauerstoffverbrauch der Papierproben gemessen werden kann. Die Proben waren nach fünf verschiedenen Neutralisierungsverfahren behandelt worden: Battelle, Bookkeeper, DEZ, FMC and Sablé. Ziel der Untersuchung war es, den Abbaumechanismus zu beschreiben, d.h. die Wirkung von Mg und Zn, die bei den Neutralisierungsbehandlungen in die Proben eingebracht werden, auf den lichtinduzierten Abbau. Um diesen zu beschleunigen, wurde der Versuch in reinem Sauerstoff, bei erhöhter Temperatur und starker Beleuchtung durchgeführt. Mit Infratrotanalyse sowie mechanischen und physikalischen Prüfverfahren wurde gezeigt, daß bestimmte Substanzen die lichtinduzierte Vergilbung verstärken. Untersucht wurden auch die oxidative Ringspaltung und der Bruch der Makromolekülkette.

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Effect of Trehalose Treatment on Paper Stability

Preliminary Experiments

by ANTONIO ZAPPALÀ, CAROLINA CANTONI, DANIELA PALAZZI, EUGENIO VITRANO & LORENZO CORDONE

Introduction

Some organisms, living in the desert, can withstand extreme dehydration and high temperatures (>60°C), without suffering damage, in a state of suspended animation, known as *anhydrobiosis*. Under such conditions, these organisms can survive for several years with the complete absence of metabolic processes; however, following rehydration, their vegetative cycle restarts. In this dry state these organisms contain large concentrations of sugars, particularly trehalose (a disaccharide composed of two linked α,α units of glucopyranose), which purports to be the most active saccaride for the preservation of biostructures[1, 2, 3].

It has been suggested that trehalose can build up hydrogen bonds to biostructures, like polar groups of membranes or OH-groups of proteins, thus replacing water. According to this hypothesis, first developed for explaining the preservation of biomembranes, trehalose replaces the hydration water at the biostructure-fluid interface, thus maintaining the polar or OH-groups at their hydrated position. This hypothesis has been supported by calorimetric and NMR (Nuclear Magnetic Resonance) data[4]; accordingly, biostructures embedded in a trehalose matrix are kept rigid and solid-like and so preventing the formation of damage due to adverse ambient conditions[2].

Moreover, recent studies[5, 6] have shown that the low frequency dynamics of carbon monoxy myoglobin, embedded in a dry trehalose matrix, measured by optical, Mössbauer and neutron spectroscopies, approach those of a harmonic solid (in which the atoms perform only small amplitude sinusoidal oscillations) up to room temperature. This is in contrast to hydrated myoglobin in which a dynamic transition to a non-harmonic regime has been observed at about 180K[7, 8, 9]. This transition is evidenced by the appearance of large-scale fluctuations in the atomic positions, likely related with the protein function.

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The observed stabilising effect of trehalose, led us to consider and evaluate whether this sugar might also be a potential stabiliser for paper. For this purpose we performed some experiments comparing different kinds of paper before and after accelerated ageing, some of which had been previously treated with trehalose. The aim was to investigate whether trehalose can have a protective effect on paper, by inhibiting oxidative degradation and hydrolysis reactions of cellulose, which cause a rapid decrease in the mechanical resistance of paper. It seemed possible that trehalose could slow down the natural ageing process, thus increasing the longevity of paper before it reached a level of fragility that makes the normal use of a document difficult. Paper for books and documents, particularly that produced during the last two centuries and stored in archives and libraries, frequently has poor mechanical properties so that consultation is often impossible without risking serious damage.

MATERIALS AND METHOD

Three types of paper were used for our tests:

- Filter paper Whatman no.1, a pure cellulose paper, not sized and not containing any filler of mineral origin. Such a material is an apt standard to test cellulose, which is the substance responsible for providing the mechanical strength of paper.
- Acidic sized paper, prepared by grinding samples of Whatman no. 1 in an aqueous suspension, adding rosin and alum, at pH4, before felt forming.
- Unsized acidic paper (pH4), obtained by soaking Whatman 1 paper in diluted sulphuric acid.

For these three kinds of paper several different samples were prepared by soaking in aqueous solutions of trehalose of increasing concentrations: 0.2M, 0.5M, 1M.

Altogether, the following samples were prepared:

- Whatman no.1, not treated
- ... treated with trehalose 0.2M
- ... treated with trehalose 0.5M
- ... acidified with H_2S0_4
- ... acidified with H_2S0_4 and treated with trehalose 0.2M
- ... acidified with H_2S0_4 and treated with trehalose 0.5M

- ... acidified with H_2S0_4 and treated with trehalose 1M
- ... sized with alum-precipitated rosin
- ... sized with alum-precipitated rosin and treated with trehalose 0.2M
- ... sized with alum-precipitated rosin and treated with trehalose 1M

Each of these ten samples – after drying – were cut into two halves: one of them was kept for 25 days in a climatic test chamber (Votsch VC 2033) at 80°C and 65% RH, in order to obtain a rapid artificially aged sample; the second half was kept under normal environmental conditions, as a control.

The stability of the samples was evaluated by means of the following measurements:

- Measurement of degree of polymerisation (DP) of cellulose, according to the French method AFNOR T 12-005, i.e. by measuring the flowing time of sample solutions in cupriethylenediamine, in a standard capillary viscosimeter. An estimated percentage content of trehalose and a further 6% attributed to the average quantity of water present at 25°C and 60% RH were subtracted from the sample weight.
- Surface pH measurement of paper, using a pH-meter with flat membrane electrode; measurements were performed by surface contact.
- Measurements of the variation of colour defining parameters (co-ordinates CIE L* a* b*), using a portable spectrophotometer Minolta Chroma Meter CR221. Colour co-ordinates are defined as follows:
  - L* is the brilliance. It is represented by the vertical axis, perpendicular to the plane defined by the two a* and b* axes, and it varies from 0 (dark) to 100 (clear).
  - a* is the red-green axis. Positive values from 0 to 60 indicate a colour which is on the reddish side, negative values from 0 to -60, indicate a colour which tends to be green,
  - b* is the yellow-blue axis. It ranges from strong yellow (+60) to blue (-60).

In this colour space, white is theoretically the point of co-ordinate L*=100, a* = 0, b* = 0. In measurements on paper samples, the most important parameters are L* and b*. A decrease of L* indicates a loss of brilliance, i.e. a slight displacement towards grey; a variation of b* from slightly negative to positive values indicates yellowing.

For each sample four measurements were taken in four different places (two on each side); each value resulted from the average of three consecutive measurements, automatically performed by the instrument.

RESULTS

Before describing the results, we think it is worth mentioning that the paper rigidity increases by increasing the trehalose concentration.

Degree of polymerisation (DP) measurements

We first determined the trehalose content of the samples. This was performed by assuming uniform thickness of Whatman paper and by comparing the weight of untreated samples with the weight of samples of equal surface area treated with different trehalose concentrations. This method allowed us to observe that both, untreated Whatman paper and sulphuric acid treated paper absorbed, approximately, the same percentage of trehalose. The laboratory hand-made alum-rosin sized paper was inhomogeneous in thickness, which made it impossible to use the above method for weight correction.

The following amounts of trehalose were absorbed:

- Trehalose 1M: ca. 38 %
- Trehalose 0.5M: ca. 25 %
- Trehalose 0.2M: ca. 12 %

The results of DP measurements obtained on all the paper samples used are given in Table 1.

It can be seen that trehalose treatment has virtually no influence on the decrease of DP during the ageing of non-acid paper. For alum-rosin sized paper treatment with trehalose seems to have a significant protective effect. Moreover, it can be seen that the protective effect is not related to the amount of trehalose deposited on the fibres: it is nearly the same with the paper treated with 0.2M and with 1M trehalose solutions. A protective effect, resulting from trehalose treatment and not depending on the amount of trehalose deposited on fibres, is also evident on the sulphuric acid treated samples.

Table 1: Degree of polymerization for samples, before and after accelerated ageing.

	trehalose							
	–		0.2M		0.5M		1M	
	unaged	aged	unaged	aged	unaged	aged	unaged	aged
no pre-treatment	1056	784	1029	764	992	757	–	–
pre-treated with H_2SO_4	996	577	1014	713	997	750	941	664
alum-rosin sized, pH4	719	183	585	214	–	–	600	224

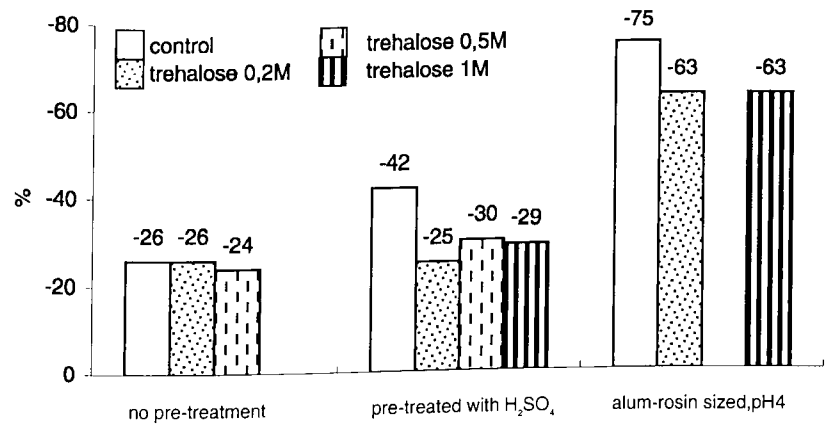

Fig. 1: ΔDP %, i.e. (DP aged/DP unaged x 100) – 100. Unaged = 0.

A graphic representation of the results obtained is given in Fig. 1. The histogram summarizes DP data of artificially aged, unaged, treated and untreated samples.

Data in Table 1 show that before artificial ageing, the DP of unsized Whatman paper samples (not acidified and sulphuric acid acidified, trehalose treated and untreated) is about 1000. Laboratory made alum-rosin sized paper samples, however, have lower DPs, most likely due to the grinding that was part of the production process of these samples.

The DP decrease during accelerated ageing of untreated Whatman paper is the same (~ 25%), whether this paper has been treated with trehalose in different amounts or not (Fig. 1). A slightly stabilising effect as a result of a trehalose treatment is evident with acidic paper. The treatment with trehalose solution 0.2M gives the best results with sulphuric acid treated paper. As the artificially aged and unaged samples are the two halves of the same sheet; the observed DP ratio decrease is thus significant.

pH measurements

The results of pH measurements are given in Table 2.

Comparing the values of artificially aged samples with those of the respective unaged samples, some very small trehalose effects seem to appear. Non-acidified Whatman 1 paper shows a slight pH decrease after ageing, which is more relevant for the untreated sample, lower for the sample treated with trehalose 0.2M and nearly nothing for the sample treated with 0.5M trehalose. Even sulphuric

Table 2: pH values for samples, before and after artificial ageing

	trehalose							
	–		0.2M		0.5M		1M	
	unaged	aged	unaged	aged	unaged	aged	unaged	aged
no pre-treatment	6.3	5.6	6.0	5.7	6.2	6.1	–	–
pre-treated with H_2S0_4	5.1	5.2	4.7	4.8	5.2	5.6	5.0	5.4
alum-rosin sized, pH4	4.5	4.3	4.0	3.9	–	–	4.6	4.7

Table 3: CIE L*, i.e. "brilliance" of samples treated with trehalose, before and after accelerated ageing.

	trehalose							
	–		0,2M		0,5M		1M	
	unaged	aged	unaged	aged	unaged	aged	unaged	aged
no pre-treatment	94.71	93.58	94.83	94.36	94.61	94.10	–	–
ΔL* (unaged – aged)	–	-1.13	–	-0.47	–	-0.51	–	–
pre-treated with H_2S0_4	94.73	93.37	94.76	94.17	94.60	93.80	93.73	93.40
ΔL* (unaged – aged)	–	-1.36	–	-0.59	–	-0.80	–	-0.33
alum-rosin sized, pH4	92.70	78.90	93.80	80.70	–	–	93.37	82.80
ΔL* (unaged – aged)	–	-13.80	–	-13.10	–	–	–	-10.57

acid acidified samples, treated with trehalose 1M and 0.5M seem to exhibit, following accelerated ageing, a slight pH increase. There appear to be no effects on samples of paper sized with rosin and alum. Generally, trehalose seems to have a slightly stabilizing effect on pH change during accelerated ageing.

Colour measurements

Table 3 gives the numbers for CIE L* of samples treated with trehalose, before and after ageing.

Treatment with alum and rosin causes a slight decrease of brilliance (94.71 → 92.70 = -1.97), even before accelerated ageing, and is significantly greater after ageing. Trehalose treatment of 0.2 M and to a greater extent of 1M slightly reduces this effect. For unpretreated pure cellulose paper (Whatman no. 1) and the acidified samples it can be stated that, generally, trehalose treatment, in whatever concentration, does not significantly influence the actual brilliance, but it does have a slight stabilizing effect on brilliance during accelerated ageing.

Table 4 gives the results of the measurements of a*, Table 5 the results of b* parameters, Fig. 2 the latter in graphic form. It can be seen that there is little in-

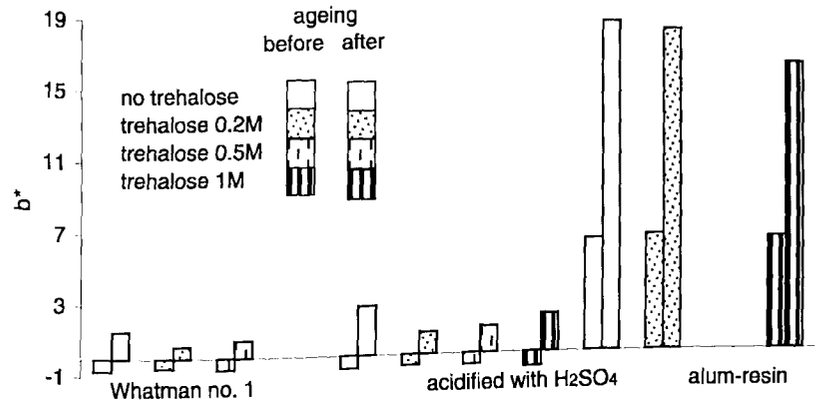

Fig. 2: Colour measurement: CIE b* of treated and untreated samples before and after accelerated ageing.

Table 4: CIE a* of treated and untreated samples before and after accelerated ageing.

	trehalose							
	–		0.2M		0.5M		1M	
	unaged	aged	unaged	aged	unaged	aged	unaged	aged
no pre-treatment	0.49	0.37	0.43	0.35	0.50	0.32	–	–
Δa* (aged – unaged)	–	-0.12	–	-0.08	–	-0.18	–	–
pre-treated with H_2S0_4	0.45	0.25	0.41	0.30	0.49	0.27	0.65	0.33
Δa* (aged – unaged)	–	-0.20	–	-0.11	–	-0.22	–	-0.32
alum-rosin sized, pH4; a*	-1.12	2.25	-1.10	1.67	–	–	-1.13	1.16
Δa* (aged – unaged)	–	3.37	–	2.77	–	–	–	2.29

Table 5: CIE b* of treated and untreated samples, i.e. yellowing of samples treated with trehalose, before and after accelerated ageing.

	trehalose							
	–		0,2M		0,5M		1M	
	unaged	aged	unaged	aged	unaged	aged	unaged	aged
no pre-treatment	-0.68	1.54	-0.55	0.71	-0.64	1.00	–	–
Δb* (aged – unaged)	–	2.22	–	1.26	–	1.64	–	–
pre-treated with H_2S0_4	-0.72	2.78	-0.59	1.26	-0.66	1.53	-0.84	2.15
Δb* (aged – unaged)	–	3.50	–	185	–	2.19	–	2.99
alum-rosin sized, pH4; b*	6.30	18.50	6.50	18.00	–	–	6.32	16.00
Δb* (aged – unaged)	–	12.20	–	11.50	–	–	–	9.68

fluence of the trehalose treatment on either colour parameters. A slightly lower yellowing as a result of trehalose treatment may be seen, and, moreover, the lower the trehalose concentration the lower the yellowing before and even more after

accelerated ageing. The contrast is true for the comparatively high yellowing of alum-rosin sized samples. It must be noted that these samples are inhomogeneous and exhibit an irregular surface.

Conclusions

The results presented here do not enable a clear cut interpretation of the effects of trehalose on paper stability. However, it is worth noticing that the following trends can be stated:

- Untreated Whatman paper:
  Treatment with trehalose has virtually no influence on the decrease of DP during accelerated ageing. Change of colour during ageing both for L* and for b* values is less in trehalose treated samples. Trehalose also seems to limit a decrease in pH during ageing.
- Sulphuric acid treated Whatman paper:
  Accelerated ageing seems to bring about a lower decrease of DP in trehalose treated paper; the observed effect does not depend on the concentration of trehalose. Colour co-ordinates L* and b* undergo lower variation in trehalose treated paper and trehalose seems not to affect paper pH.
- Alum-rosin sized paper:
  Also in this kind of paper trehalose reduces ageing induced depolymerisation. Trehalose also seems to reduce the loss of brilliance (CIE L*) and the yellowing (CIE b*) caused by accelerated ageing. The pH is not affected.

The observed results suggest a continued study of the effect of trehalose on paper, particularly if it was extended to include samples of old papers of different composition, as they are found in archives and libraries. This first attempt to study the stabilising effects of trehalose on paper suggests it may be worth while considering an eventual synergy between the positive effect of trehalose on the preservation of precious ancient documents and that brought about by deacidifying compounds, which are generally used in the conservation of books and documents. If this proves to be true, then it might be possible to combine the usual deacidification processes with a trehalose treatment.

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Summaries

Effect of Trehalose Treatment on Paper Stability. Preliminary Experiment

Trehalose, a non-reducing disaccharide, is supposed to be responsible for the survival of anhydrobiotic organisms when under stress. This sugar prohibits the formation of damage during adverse external conditions such as extremely high temperature or dehydration. In this paper we report preliminary experiments on paper stabilisation by treatment with trehalose; the experimental results are encouraging and suggest further study on this topic would be worthwhile.

Effet du traitement au tréhalose sur la stabilité du papier. Une expérience préliminaire

On attribue au tréhalose, un disaccharide non-réducteur, un rôle décisif dans la stratégie de survie de certains organismes anhydrobiotiques placés dans des conditions extrêmes de chaleur et de sécheresse. En effet ce sucre permet d'éviter les dégâts susceptibles de se produire en conséquence de conditions externes défavorables, telles qu'une température caniculaire et une déshydratation. Dans cet article nous présentons les premières expériences portant sur la stabilisation du papier réalisées au moyen de tréhalose. Les résultats obtenus sont encourageants et permettent de supposer qu'il serait intéressant de poursuivre les recherches sur ce sujet.

Die Beeinflussung der Stabilität von Papier durch Trehalose. Eine vorläufige Untersuchung

Trehalose, einem nicht-reduzierenden Disaccharid, wird eine entscheidende Funktion in der Überlebensstrategie von Wüstenpflanzen in Zeiten großer Hitze und Wassermangel zugeschrieben. In der Tat verhindert dieser Zucker Schäden, die als Folge ungünstiger Bedingungen wie hohe Temperatur und Wasserentzug auftreten. Es wird über erste Versuche zur Stabilisierung von Papier durch Trehalose berichtet. Die Ergebnisse ermutigen zu weiterführenden Untersuchungen.

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Cellulose Viscometric Oxidometry

by LUDOVICO SANTUCCI & MARIAGRAZIA PLOSSI ZAPPALÀ

Introduction

The difficult job of scientific advisors in the field of paper conservation would certainly benefit from improved methods of characterizing cellulose degradation. The complexity and variability of paper composition and its structure hampers exhaustive and generally valid descriptions of the attendant processes. Here we deal only with papers consisting mainly of cellulose.

Even papers considered to be pure cellulose felts are seldom simple systems, they often contain various additives and impurities, for example, cellulose is usually accompanied by small amounts of hemicelluloses and pectins. We found more than traces of alkaline carbonates even in Whatman No. 1 chromatography paper[1], together with minor amounts of iron and copper compounds.

The approach to chemical solutions and an understanding of the problem must therefore consist of a succession of small steps. Acidity has been investigated extensively since the 1930s; the degree of oxidation somewhat less so, i.e., the extent of the conversion of alcoholic groups to carbonyls or carboxyls. Fundamental and industrial chemistry have shown the connection between the strength of a paper sheet and the length of cellulose chains. It has been further shown that oxidized sites along the chain are weak, easily attacked by acids and bases, which consequently cause the cleavage of nearby glycosidic links between (anhydro) glucose chain units.

Therefore, we could say that, while chain shortness in itself, although affecting the present properties of paper, does not necessarily impair its useful life expectancy, oxidation can. Information as to the degree of oxidization is thus important; particularly for conservator-restorers, whose decisions about treatment may well be influenced by this knowledge. But when can we say some paper is oxidized? It is a common belief that brown papers are, and sometimes this is true. But the colour may be due to compounds other than cellulose[2], or it may be due to some surface alteration: very small amounts of dark substances can cause discoloration. It is commonly reputed that visible damage is caused by conjugated unsaturation, often produced by the well-known proton-activated olefin

formation from alcoholic groups, especially in hemicelluloses. An excellent review on this topic appeared in 1993 in this journal[3].

In principle, the problem of measuring the degree of oxidation of a cellulose sample has been solved. Well known techniques range from approximate optical determinations or other non-destructive methods[4-11] to the titration of specific groups, but the latter usually being destructive procedures. Of course, non-destructive methods are more appropriate for diagnostic purposes, but all methods of oxidation measurement help research into cellulose degradation, allowing us to correlate oxidation to paper stability. This involves, above all, carbonyl (keto and aldehyde groups) and carboxyl determinations. The latter are easily determined by titration, or by the methylene blue procedure when bound to chains long enough to be insoluble; however, they are not as destabilizing as carbonyls.

Dangerous carbonyls are those which are distributed along chains, not those on the end groups. Unfortunately, most analytical methods cannot differentiate end groups from the others. Only sophisticated, time-consuming and sometimes rather dangerous techniques allow this[12-13]. It is similarly problematic to differentiate between keto and aldehyde groups[14-17]. Simpler copper-number, HAS (Hot Alkali Soluble) matter[18] and free-radical determination[19] certainly give useful indications but these have a limited quantitative significance.

Recently, a simple and elegant solution was suggested by Whitmore and Bogaard[20, 21] improving the HAS-based method[18] previously suggested by the same school; they estimated end groups by the DP (degree of polymerization) value, and determined side carbonyls by subtracting end groups from a total carbonyl determination. Applying this method to the results of four different artificial ageing procedures, Whitmore and Bogaard, save for two exceptions, found no carbonyl production in excess of the increase of end units, thus ruling out any oxidative effect of artificial ageing on pure cellulose paper. Agreement among investigators on this matter is not unanimous[22-25]. For example, according to Arney and Jacobs[26], an oxygen-depending process coexists during degradation with an oxygen-independent one.

However, several other researchers have concluded in favour of predominantly hydrolytic degradation. Our findings also agreed with Whitmore's conclusions when we examined, through a somewhat similar viewpoint, the effect of magnesium bicarbonate deacidification[27]. In another instance, however, applying Whitmore's method to previous data, we found definite evidence of cellulose oxidation. Paper heated for 18 days at 95°C in a *sealed tube* contained an excess of over 5 mmoles/100 g of carbonyls with respect to merely hydrolytic increase of end groups[28].

Most of our previous data, when concerning treatments, which are not specifically oxidative, do not show evidence of cellulose oxidation through ageing by

this criterion, in agreement with Whitmore's findings. We had expected instead to observe oxidation when ageing paper containing substantial amounts of sodium carbonate[1, 29], because it depolymerized, dropped in pH and yellowed at a fast rate. However, the modest carbonyl excess did not substantiate this view. It should be noted that in more than one run the carbonyl content was seen to pass through a maximum. It is therefore possible that carbonyl groups were destroyed by β-alkoxy elimination reaction as soon as they were produced. Peeling being unlikely to cause such a sharp fall in DP, those results may well mean that the end products of oxidative degradation were rather carboxyls, attached to soluble fragments (undetectable by the methylene blue method, but evidenced by a pH drop).

Apparently, such facts show that oxidometry methods, based on the presence of non-end carbonyls, may not necessarily rule out an oxidative route in cellulose degradation, in addition to not accounting for the presence of carboxyls. We did not further pursue investigation of decomposing carbonyls. However, here we suggest a fast procedure to evaluate approximately cellulose oxidation, which will be shown to differentiate oxidized samples from samples devoid of carbonyls along the chain. This method apparently also allows the separation of mere hydrolytic or at least direct chain cleavages from scissions made possible by oxidation.

Suspicion that DP of alkalinised paper drops on ageing, as mentioned above[1, 29], might not be due to weak links or peeling reactions alone, but rather to β-alkoxy elimination rapidly following oxidation of alcoholic groups to carbonyls in a basic environment, led us to try and exploit the latter reaction for estimating the degree of oxidation of cellulose[30], by a procedure somewhat different from HAS content. It is known that scissions of glycosidic bonds activated by β-carbonyls in a basic environment proceed at considerably fast rates, and drastically influence average DP. Therefore, it should be possible to estimate the extent of the oxidation of a cellulose sample by artificially causing the cleavage reactions and then comparing the resulting DP with the original one. Converting viscometric values of DP to the more significant number average DP_n, within certain limits and approximations[31,32] the expression $1/DP^h - 1/DP$, where DP^h is the degree of polymerization measured after heating the sample (see below: Experimental), yields a measure of bond scissions which occur during a given process. If care is taken to compare DP values concerning only the cleavage process just mentioned, a measure of cellulose degree of oxidation is obtained. A preliminary application of this method has already been reported[33].

It will be shown here how this is possible by comparing the DP of an oxidized sample heated under nitrogen in the same (alkaline) solvent used for viscometry, with the original DP before heating. This of course, will not account for possible carboxyl formation: but carboxyl formation can be easily determined in other ways.

EXPERIMENTAL

Materials and method

Whatman n° 1 chromatography paper was used as a starting material throughout.

- Hydrolysis. Hydrocellulose samples (Table 2) were obtained by heating at 80°C 1 g of Whatman paper in 150 ml of 0.1 N HCl, in a condenser-equipped vessel, varying the duration of treatment. Pure Nitrogen was bubbled through the suspension, starting 15 min before heating began, in order to prevent concurrent oxidation.
- Oxidation. Samples were oxidized by immersion in aqueous solutions of KIO_4 or NaClO. Concentrations of oxidants and treatment duration are shown in Tables 3 and 4. All samples were always thoroughly washed in demineralized and distilled water after treatment.
- Reduction. Samples were reduced by immersion in aqueous solutions of borane derivatives. Concentrations of reducers and treatment duration are shown in Tables 3 and 4. All samples were always thoroughly washed after treatment. Sodium borohydride was not used in case its alkalinity might cleave chains before reduction.

MEASUREMENTS

Average viscometric degree of polymerization (DP_v)

Average viscometric degrees of polymerization (DP_v) are listed in Tables 1–4 as determined both on the samples either untreated or oxidized, and on the same samples after reduction: the latter values are more significant, as explained further on.

- "Cold" DP_v. After conditioning samples for at least 3 days at 23°C and 50 % R.H., DP was determined according to the French Standard AFNOR T12-005, in cupriethylenediamine (CuED) at 20.0°C. Measurements usually resulted with standard deviation $\sigma = 10$.
- "Hot" DP_v , or $DP_v{}^h$. $DP_v{}^h$ was similarly measured at 20.0°C, according to the French Standard AFNOR T12-005, after the dissolved sample had been heated at 60°C to cause alkaline scissions. Heating was performed in a nitrogen atmosphere to prevent alteration of the solvent and further oxidation of

Table 1. Depolymerization as a function of heating time at 60°C of a sample oxidized by potassiun periodate.

Time (min)	DP_v in CuED solution	DP_v in 0.1N NaOH suspension
0	695	695
15	555	497
30	483	475
60	487	450
90	–	487
120	–	485

Table 2. Hydrolysis of Whatman paper with HCl 0.1N*.

Treatment	DP_v	$DP_v{}^h$
Untreated	1340	1273
hydrolysis time 15 min	879	834
hydrolysis time 30 min	638	666
hydrolysis time 60 min	517	555
hydrolysis time 120 min	443	441

* hydrolyzed at 80°C in a nitrogen atmosphere

Table 3. Hypochlorite oxidation of Whatman paper (immersion at room temperature).

Sample	Treatments	DPv not reduced	DPv reduced	$DP_v{}^h$ (heated) not reduced	$DP_v{}^h$ (heated) reduced	Heating medium*
A	none	1521	1573**	1335	–	CuED
A	NaClO 0.3% at pH 7, for 10 min	1328	1334**	1087	–	CuED
A	NaClO 0.3% at pH 7, for 20 min	903	1133**	797	–	CuED
B	none	1281	1300**	1256	1260	CuED
B	NaClO 1 % at pH 7, for 10 min	960	1044**	850	1035	CuED
B	NaClO 1 % at pH 7, for 30 min	800	880**	680	850	CuED
C	none	1367	1367**	1335	–	CuED
C	NaClO 1 % at pH 7, for 30 min+ inmin+	212	270***	179	–	CuED
C	NaClO 1 % at pH 7, for 30 min+	212	270***	189	–	NaOH++

* Used for $DP_v{}^h$ determination in nitrogen atmosphere:
CuED (cupriethylenediamine) 0.5M, heating time 30-60 min at 60°C
NaOH 0.1M, heating time 30 min at 60°C

** Reduction in $(CH_3)_3CNH_2BH_3$ 0.2M for 1 h

*** Reduction in $NaBH_3CN$ 0.2M for 3 days, buffered at pH 3.5

\+ Then naturally aged for 2 years at room temperature

++ Weight loss after 3 hrs.: 4.0 %

Table 4. Periodate oxidation of Whatman paper (immersion at room temperature).

Sample	Treatments	DPv		DP_v^h (heated)		Heating medium*
		Not reduced	Reduced	Not reduced	Reduced	
D	none	1302	1329 **	1283	1247	CuED
D	KIO_4 0.015 M, for 15'	650	1059 **	436	934	CuED
D	KIO_4 0.015 M, for 30'	425	1107 **	275	1057	CuED
D	KIO_4 0.015 M, for 2 h	315	964 **	170	955	CuED
E	none	1380	1395 **	1258	–	CuED
E	KIO_4 0.02 M, for 6 h+	695	1046 ***	483	–	CuED
E	KIO_4 0.02 M, for 6 h+	695	1046 ***	475	–	NaOH++
F	none	1347	1291	1274	–	CuED
F	KIO_4 0.4 M, for 3 h+	180	535	141	–	CuED

* Used for DP_v^h determination in nitrogen atmosphere:
CuED (cuprietylenediamine) 0.5M, heating time 30-60 min at 60°C
NaOH 0.1M, heating time 30 min at 60°C

** Reduction in $(CH_3)_3CNH_2BH_3$ 0.2M for 1 h

*** Reduction in $NaBH_3CN$ 0.2M for 3 days, buffered at pH 3.5

\+ Then naturally aged for 2 years at room temperature.

++ Weight loss after 3 hrs: 1.1 %

the sample, beginning by bubbling for 15 min before heating in order to chase out air. A condenser was used to prevent evaporation of the solvent.

The flow rate of CuED, measured at 20.0°C, was found to remain essentially constant, even after prolonged heating at 80°C.

Repeated runs on oxidized samples showed that the scission process was usually completed within 30 min at 60°C, as the DP did not appreciably decrease any more, but in most cases a heating time of 60 min at 60°C was used. However, when the sample (even those not previously oxidized) was heated for longer than 2 hours, or left overnight at room temperature, degradation resumed: possibly, by some mechanism catalyzed by copper, which was actually seen to separate onto the walls of the vessel if heating was prolonged.

The same procedure was used to heat suspensions in 0.1 N NaOH, which required about the same time of reaction. In this case, the weight loss of samples was also determined, and never found to exceed 4%, even for heating periods of 3 hours at 60°C.

Table 1 shows typical runs of samples heated in both CuED and sodium hydroxide.

Number-average degree of polymerization DP_n

The relation between the number-average degree of polymerization (DP_n), which best expresses the average length of chains, and the experimental viscosity-average degree of polymerization (DP_v), was summarized by Whitmore and Bogaard[20, 21]. They adopted approximate value 0.5 for the ratio DP_n / DP_v, as had other investigators previously. We chose to follow this procedure. This relation, however, is not in general agreement with experimental data of Immergut[34] and Lauriol[35]. Immergut measured DP_n and DP_v by independent methods and Lauriol obtained both values from GPC measurements on cellulose tricarbanylates.

Carbonyl groups content

The determination of carbonyl amount was performed with a modification of Szabolcs methodology[36-39]. 0.5 ml of KOH 0.2M and 0.5 ml of TTC (2,3,5-Triphenyltetrazolinium chloride) 0.1% w/V were added to 5-90 mg of exactly weighted paper, placed in a flask, and the resulting suspension was placed in a boiling water bath. After 10 min the solution was cooled and 0.2 ml of 1M HCl was added, otherwise the red colour of the solution (especially in the case of diluted solutions) quickly disappeared and the measurement was not reproducible. The deep red triphenylformazan precipitate was dissolved in ethyl alcohol (EtOH); the solution was filtered from residual paper and the volume sized to 20 ml with EtOH. Solution absorbance was measured at λ=480 nm, using a Perkin-Elmer Lambda-5 spectrophotometer. We want to stress that solutions of formazan must not have a water content above 10%. The amount of carbonyl in paper was measured from the calibration line, obtained using water solutions of glucose.

RESULTS AND DISCUSSION

Effect of hydrolysis, oxidation and reduction

In the Tables we compare the effect of heating in a basic environment different samples of unmodified cellulose (Whatman n°1 chromatography paper) or products of hydrolysis by 0.1N HCl, with the effect of that treatment on samples of cellulose oxidized by sodium hypochlorite or potassium periodate. Heating in a basic medium invariably caused a greater extent of depolymerization in oxidized samples than in unmodified cellulose.

Table 5. Total carbonyl group contents (including end groups) from TTC (mmoles/100 g paper).

Sample	Treatments	not reduced	reduced
A	untreated	0.52	0.45***
A	NaClO for 10 min	0.91	0.71***
B	untreated	0.54	0.47***
B	NaClO for 10 min	3.69	0.66***
B	NaClO for 30 min	6.88	0.95***
D	untreated	0.56	–
D	KIO_4 for 15 min	4.97	0.47***
E	untreated+	0.52	–
E	KIO_4 for 6 hours+	5.38	–
F	untreated+	0.54	–
F	KIO_4 for 3 hours+	22.7	–
F	KIO_4 for 3 hours+++	21.0	–

*** Reduction in *tert*-butylamine complex $(CH_3)_3CNH_2BH_3$ 0.2M for 1 h
\+ Then naturally aged for 2 years at room temperature.
+++ Hydroxylamine method, including end groups[13,14]

Several samples were also checked for their carbonyl content, in order to make sure oxidation occurred (Table 5).

We preferred to investigate the relation between oxidized sites and consequent scissions in basic rather than acidic media mainly because the solvent for viscometry itself can be used as a basic medium, but also for its possible implications on paper bleaching followed by deacidification [25, 40, 41]. It could be argued that the observed scissions were due to the weak links reported by some authors[31, 42–44]: but our data for definitely oxidized samples go well beyond the reported estimate of 0.03% of the links. Besides, heating in basic media had little effect on untreated or acid-hydrolyzed samples: few chain carbonyls might actually be responsible for whatever small variations were observed in those cases.

Hydrocellulose samples (Table 2), prepared in strictly non-oxidizing conditions (nitrogen atmosphere), appear to be quite unaffected by alkaline heating. Even the slight DP decrease observable in untreated Whatman, where a few chain carbonyls may be present is absent.

For hypochlorite oxidation, conditions were used, which were known[17] to produce a maximum of chain carbonyls and a minimum of carboxyls (pH 7); it is also known that treatment near neutral pH causes considerable depolymerization (Table 3). Neither carboxyl content nor pH were investigated, being outside the scope of this work. In a few cases chain carbonyl content was measured (Table 5), but with no effort to determine their position along the chain or to differentiate keto from aldehyde groups.

The DP drop on heating of hypochlorite-oxidized samples is quite evident. Most of these were also reduced by boron complexes treatment, which produced an appreciable rise in DP, as also reported by Burgess[41] and Feller[18]. This was explained by the degrading effect on side-oxidized chains of the alkaline solvent during viscometry operations. It is quite striking that reduced samples seem considerably more impervious to alkaline heating than oxidized samples before reduction: which confirms the role of carbonyl groups in the observed DP decrease.

Potassium periodate is supposed to be a more specific oxidant, attacking only C_2 and C_3 atoms: although whether keto, aldehyde or carboxylic groups are obtained will depend on the experimental conditions. We also observed severe depolymerization (Table 4), though subsequent reduction showed that it was in part caused by the alkalinity of CuED.

In this case, the susceptibility to alkaline heating was even greater than for hypochlorite-oxidized samples, and boron complexes reduction similarly protected chains from the basic attack. The high excess of carbonyls measured in some samples with respect to the expected increase of reducing end groups confirms the considerable extent of oxidation attained; also shown, on the other hand, by the disappearance of CO groups upon reduction (Table 5).

The value of DP_v^h was also determined in some of the samples after previous reduction (last column of results in Tables 3 and 4), in order to confirm that provoked cleavage by alkaline heating affects oxidized cellulose only. Data from these columns and the first ones of Tables 3 and 4 were not used for the evaluations discussed in the next section.

Evaluation of the extent of oxidation

The results reported here clearly show that the degree of drop in DP after heating is dependent on the extent of oxidation.

We have mentioned already the relation between number average DP before and after a depolymerization process, and the number of glycosidic bond scissions produced in that process. From now on we shall indicate with the notation DP the number average in place of the viscometric degree of polymerization, obtained from the latter by the relation $DP_n=DP_v/2$

As we pointed out above, the reduction of samples before viscometric measurements yields more significant information, because by the time the viscosity reading is carried out some additional depolymerization occurs when the sample is oxidized, by the action of the basic solvent even at 20°C. This is shown by the increased DP that reduction produces.

Now, if we consider the following values:

- DP^o_r = number-average DP of original (unoxidized) sample, but after reduction
- DP_r = number-average DP of oxidized sample, after reduction
- DP^h = number-average DP of oxidized sample, after alkaline heating

We can express a total number of scissions, which have occurred in the whole process from oxidation to the end of heating (eq. [1]), and also what happened in the process before heating was applied (eq. [2]): the latter value represents cleavages which have occurred directly on glycosidic bonds during treatments, hence not induced by solvent alkalinity on a bond in beta-position to carbonyls.

Combining such relationships we obtain:

[1] $1/DP^h - 1/DP^o$ total glycoside bond scissions

[2] $1/DP_r - 1/DP^o$ direct (essentially hydrolytic) bond scissions

[3] = [1] − [2] = $1/DP^h - 1/DP_r$ scissions induced by alkalinity near carbonyls

If we multiply the above calculations by 617*, the scissions will come to be expressed in m.mol/100 g. Obviously, no previous reduction is required to determine DP^h. A numerical example will make things clearer. For instance, in the case of sample B, oxidized 30 min by 1% hypochlorite, the above equations looks as follows:

[1] 2 (1/880 − 1/1300)617 = direct scissions = 0.45 mmol/100 g

[2] 2 (1/680 − 1/880)617 = oxidative scissions = 0.41 mmol/100 g

[3] 2 (1/680 − 1/1300)617 = total scissions = 0.86 mmol/100 g

Equation [3] ought to provide the information we had been seeking, that is a measure of the damage inflicted to cellulose by oxidation. This kind of evaluation will also hold for samples whose previous history is unknown (obviously applying only equation [3]): hence its diagnostic value.

Table 6 summarizes the results of the above calculations applied to the present experimental data (1st and 2nd column of results in Tables 3 and 4). We called values resulting from equation [3] *Oxidation Index* because they actually give an indication of the extent of oxidation; it is quite evident that such index is greater the higher the side carbonyl content.

The rate of carbonyl-induced scissions appears to be slower in hypochlorite-oxidized samples: possibly, comparing the original DP with a conventional LODP

* $617 = 100 \frac{1000 \text{ (conversion of mole to millimole)}}{162 \text{ (molecular weight of anhydroglucose unit)}}$

Table 6. Oxidation index.

Sample	Treatment	Scissions (mmol/100 g) Direct	Oxidative	Total
A	none	0	0.14	0.14
A	NaClO 0.3% pH7 20'	0.30	0.46	0.76
B	none	0	0.02	0.02
B	NaClO 0.3% pH7 10'	0.22	0.27	0.49
B	NaClO 0.3% pH7 30'	0.45	0.41	0.86
C	none	0	0.02	0.02
C	NaClO 1% pH7 30', (CuED)	3.6	2.3	6.0
C	NaClO 1% pH7 30', (NaOH)	3.6	2.0	5.6
D	none	0	0.01	0.01
D	KIO_4 0.015M pH5 15'	0.23	1.6	1.9
D	KIO_4 0.015M pH5 30'	0.19	3,4	3.6
D	KIO_4 0.015M pH5 2 hrs.	0.35	6.0	6.3
E	none	0	0.1	0.1
E	KIO_4 0.02N 6h, (CuED)	0.30	1.4	1.7
E	KIO_4 0.02N 6h, (NaOH)	0.30	1.4	1.7
F	none	0	0.1	0.1
F	KIO_4 0.4M 3 hrs.	1.4	6.5	7.9

(Leveling Off Degree of Polymerization) after oxidation and alkaline treatment at lower temperature would yield more accurate results. But it would take longer, and anyway the present procedure provides an estimate of the initial tendency of oxidized cellulose to degrade, although further investigation would certainly be desirable.

It could be expected that the same number of scissions as of the CO groups present could be found, since potentially every CO can break a glycoside bond in β-position. Of course, the number of inactive aldehydic end groups should be subtracted from the total carbonyl content as determined by titration (it can be assumed the number of reducing end groups is statistically given, always using number-average DP, by 617/DP). However, in the case of periodate oxidation, two carbonyls are probably required for each scission, because of their expected proximity. There might be more than one hydroxyl on a single glycopyranose ring oxidized by hypochlorite, however, whatever their number on a single ring, only one scission would result.

If this is the case, measurable carbonyl contents, even corrected for end groups, would be in excess of dangerous carbonyls, i.e., of those capable to induce fast chain cleavage; apparently, we need not worry much about the total titrable COs. A significant index of oxidation thus appears to be rather related to DP drop induced by artificial cleavage of the oxidized sample to a constant DP.

Conclusions

It was shown that heating (at moderate temperatures) oxidized cellulose samples in CuED solvent has the same effect as heating them in dilute NaOH suspension, whereas hydrocellulose samples or samples previously reduced with boron complexes were substantially impervious to alkaline heating. The resulting DP drop can be used to estimate the number of chain links made susceptible by oxidation to further attack (*Oxidation Index*).

Viscometric measurements only are required for the estimation. This method of oxidometry is destructive in nature, but considering the small amount of material involved (20 to 40 mg) it could be applied in some cases even to authentic paper documents, if made solely of cellulose. A rough estimate can be obtained by a single sample, measuring its DP before and after heating it in the alkaline solvent, but for a more reliable evaluation it is preferable to compare its final DP with that of another sample subjected to reduction before dissolving in CuED. When applicable, this procedure may be useful as a diagnostic tool.

Besides, when investigations about the effect of treatments on cellulose paper are carried out, manipulating as shown initial and final degrees of polymerization of samples also allows the separations of scissions due to oxidation from those of a merely hydrolytic nature.

This method does not detect carboxyls and is apparently less sensitive and accurate in determining carbonyls than titration with specific reagents, probably because of the polymeric nature of cellulose: but it is quicker.

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Summaries

Cellulose Viscometric Oxidometry

It is suggested that the depolymerization of oxidized cellulose (e.g. paper) caused by alkalinity can be exploited to evaluate its degree of oxidation. A rough estimate can be obtained with just one sample measured before and after heating in the alkaline solvent for viscosity itself; a more accurate evaluation requires reduction of the sample prior to the viscometric measurement. This procedure should not be identified with determinations of total carbonyl and carboxyl contents

Mesure de la viscosité pour évaluer le degré d'oxydation de la cellulose

Ici on a proposé d'exploiter la dépolymérisation de la cellulose oxydée (du papier) causée par l'alcalinité, pour évaluer son degré d'oxydation. Il est possible d'obtenir une estimation approximative en mesurant la viscosité d'un seul échantillon avant et après l'avoir chauffé dans une solution alcaline appropriée; pour obtenir des résultats plus précis l'échantillon doit être soumis à une réduction avant que la mesure de viscosité soit effectuée. La méthode n'est pas adaptée pour déterminer la teneur globale en groupes carbonyles et carboxyles.

Cellulose Viscometric Oxidometry

Es wird vorgeschlagen, die durch Alkalisierung bewirkte Depolymerisierung von oxidierter Cellulose in Papier zur Beschreibung ihres Oxidationsgrades heranzuziehen. Eine ungefähre Abschätzung desselben kann erreicht werden durch Messen der Viskosität einer einzigen Probe vor und nach der Behandlung in der heißen alkalischen Meßlösung; für eine genauere Messung muß die Probe vor der Viskositätsmessung einer Reduktion unterworfen werden. Die Methode ist nicht geeignet zur Bestimmung des gesamten Gehalts an Carbonyl- und Carboxylgruppen.

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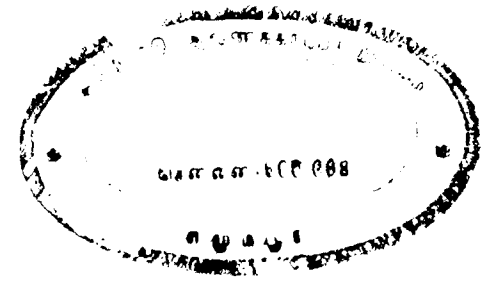

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