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Degradation of Cellulose at the Wet/Dry Interface

II. An Approach to the Identification of the Oxidation Compounds

by A.-L. DUPONT

INTRODUCTION

The problem of water-stained cellulosic material is often encountered by paper and textile conservators. The nature of the degradation compounds formed from the oxidation at the wet/dry interface is still partly unknown. Early studies on brown lines arising from the dye and textile industry are briefly reviewed. The study of the formation of brown lines on pure cellulose paper, including the effect of ageing and the effect of washing and reduction with sodium borohydride was the object of part I of this study.[1] In this previous study, the degradation was evaluated qualitatively by observation of the brown lines under natural daylight, under ultraviolet light (UV) at 366 nm and observation of their methylene blue absorption. The results showed that any wet/dry interface, even in brief exposure, may be a potential cause of degradation. Local wetting treatments seemed to be potentially harmful to paper artifacts, as for instance the removal of stains with sólvents or the use of the suction table. Ageing led to the darkening of the brown line and in the insolubility of the brown compounds. It was also showed that degradation not only leads to distinct compounds cleaved from the cellulose chain but also to oxidized cellulose with new end-groups attached to the macromolecule. The compounds formed at the wet/dry interface were described as containing carbonyl and acid groups. The purpose of part II is to further identify the oxidation compounds formed at the wet/dry interface of pure cellulose Whatman filter paper no. 5. Analysis techniques such as thin-layer chromatography (TLC), Fourier transform infrared spectroscopy (FTIR) and gas chromatography coupled to mass spectrometry (GC/MS) are used. Their advantages and drawbacks for the identification of the degradation compounds of the wet/dry interface are discussed.

BACKGROUND

In 1934 Bone[2] made the first published observation on evaporation of water from cellulose: when a strip of pure bleached cotton is dipped with one end into pure water, a brown line develops at the wet/dry interface.

In 1950, Bone & Turner[3] reported several properties of the brown lines formed on pure cotton cloth. They found that brown lines contained acid and carbonyl groups, fluoresced under UV light and caused a localized decrease in degree of polymerization (DP) of cellulose. They showed that the brown stains could be partially removed by washing in hot water or ethanol. Even after washing, the presence of acidic end-groups and the decrease in DP still was noted at the location of the water-line. The results indicated that the cellulose chain had been modified, probably to cellulose in an oxidized form. They showed that the brown products appeared to be formed by the evaporative process rather than to be due to the chromatographic migration of impurities.

The presence of oxidized cellulose of the reducing type along the brown line of a water stain was confirmed by Bogaty et al.[4] Their experiments using the fungus *Aspergillus niger* showed a preferential growth along the brown line before expanding to other areas of the pure cotton cloth. They assumed the presence of readily oxidizable compounds such as primary or secondary alcohols, probably polyols, hydroxy acids, glucose and glucose derivatives. The presence of hexuronic acids, formaldehyde and formic acid was also detected in the extract.

The role of oxygen in the formation of brown lines was investigated by Madaras & Turner.[5] Experiments carried out under vacuum showed that the formation of the brown color was inhibited while oxidized cellulose of the acidic type still was evidenced.

Schaffer et al.[6] showed that brown lines formed on cotton at the interface between air and organic solvents (benzene, xylene, chloroform, *n*-pentane). Subsequent solubility experiments showed that those brown lines on cotton obtained with solvents were soluble only in the solvent which originated them. They also showed the absence of acidic groups at the former brown line location after washing in the solvent. Cellulose chains appeared to remain unchanged.

A complementary study by Fox[7,8] reported that the freshly prepared aqueous brown line extract was acidic and that there was the exclusive presence of the elements C, H and O in the brown line products (no S, N, halogens or metals were detected). The presence of glucuronic acid was detected in the extract and the enhanced presence of carbonyls was proved. Some loss of strength at the brown line location was found after ageing under dry conditions. The infrared spectra of the brown products extracted from brown lines did not confirm the presence of glucuronic acids but showed absorption bands of inorganic salt of a carboxylic acid and bands due to long-chain aliphatic compounds and probably aliphatic ether groups. A brown line experiment on cellulose acetate and cellulose triacetate showed the formation of slight browning and slight fluorescence on the diacetate while no browning was observed on the triacetate. Both secondary and primary hydroxyl groups of the cellulose seemed to take part in the browning reaction.

All these early publications investigated several conditions under which the brown lines form at wet/dry interfaces on cotton cellulose and tried to identify the brown products. Oxidation reactions which involve the presence of oxygen are a common source of browning. The presence of carbonyl and acid groups either in small molecules fragmented from the cellulose chain, or as new end-groups on the cellulose chain formed during the process, all giving rise to browning evidence oxidation. However, the mechanism of the formation of brown lines was not totally elucidated, and all the conclusions drawn were considered as still speculative.

Browning is produced by the formation of unsaturated compounds with conjugated double bonds. Most chemical systems in which browning occurs contain carbonyl or potential carbonyl groups as the reducing sugars (sugars in their linear form), which are further transformed into unsaturated colored compounds. The fluorogens are thought to be precursors of browning.[9] More precisely, browning reactions occur in systems in which α-hydroxycarbonyl (or α-aminocarbonyl) compounds are transformed into unsaturated colored polymers. The polyhydroxy compounds are ones in which the carbonyl group is blocked, as the sugars in their cyclic form do not directly give rise to browning. First they should undergo oxidation. From the examination of the formula of the anhydroglucose unit of the macromolecule of cellulose in Fig. 1, there could be six major types of attack.[10]

1. Attack on C 1 has been shown to occur only on the terminal anhydroglucose unit. Oxidation at position 1 would result in the formation of a carboxyl group to give an acidic oxidized cellulose.

2. Attack at the 2- and 3-OH groups, either simultaneously or individually, to form carbonyl groups without ring cleavage. In this case, an oxidized cellulose of the reducing type is produced.

3. Attack at the 2- and 3-OH groups simultaneously with subsequent ring cleavage to form aldehyde groups, again leading to a reducing type of oxidized cellulose.

4. Attack on the aldehyde groups produced by reaction 3 to convert them into carboxyl groups, thus resulting in an acidic type of oxidized cellulose.

5. Attack at position 6 to form an aldehyde group which yields a reducing-type oxidized cellulose.

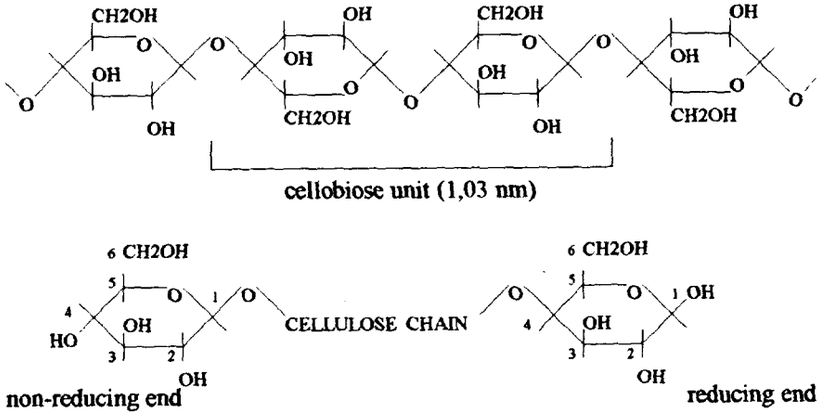


Fig. 1. Formula of cellulose.

6. Attack at position 6 to form a carboxyl group which yields an acidic-type oxidized cellulose. Fig. 2 shows the different reactions described above.

Materials and methods

Extraction of the degradation compounds from the samples

Samples were allowed to stand with the lower portion (the bottom 1-2 cm) in distilled water for 16 to 24 hours and were next dried hanging vertically. The brown lines were cut out from the papers, cut in small pieces (0.5 cm) and extracted in doubly distilled water at 50-60°C. The crude extract containing a certain amount of paper fibres was next centrifuged (2000 rpm for 10 minutes). The supernatant was then filtered using a 45-µm pore size filter (Millipore) in order to remove any residual fibers. Finally the extract either was concentrated to smaller volume or dried under N_2 flow at 40°C or under vacuum on P_2O_5 (moisture absorber). Aqueous and dry extracts were kept at 4°C.

TLC of the degradation compounds

TLC plates used were silica gel 60 plates (Merck). Two combinations of solvent mixtures for development and reagents for visualisation were used. In combination 1, development was done with the mixture *n*-butanol/ethanol/water (5:5:4) (Prosek in Sherma & Fried[11]). Visualization was done by immersion in a solution made of a mixture of naphthoresorcinol (= 1,3-dihydroxy-

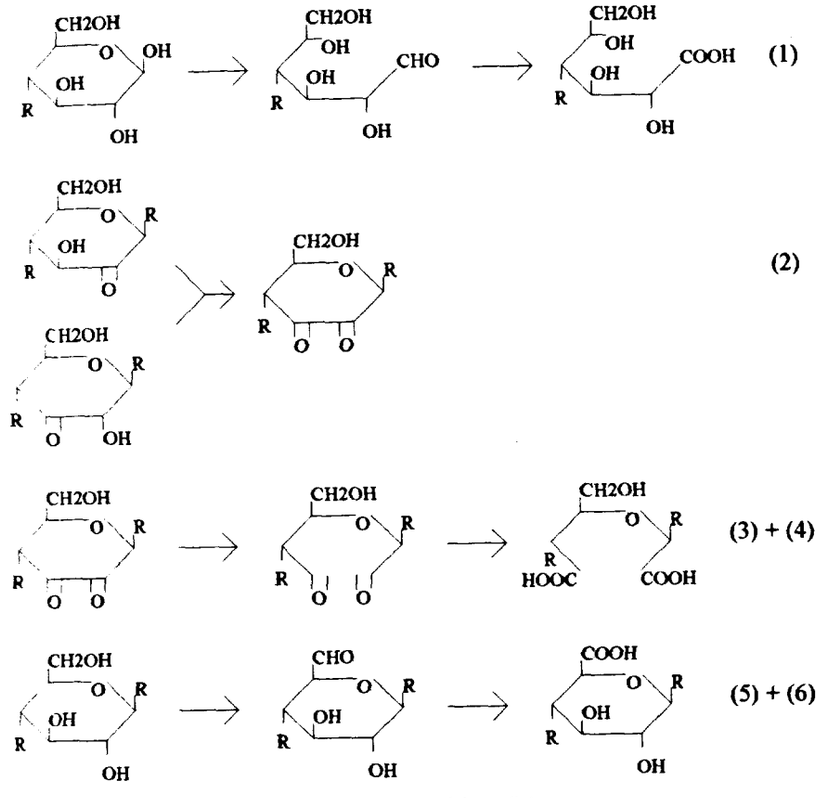


Fig. 2. Scheme of the 6 possible oxidative attacks of the cellulose.

naphtalene) (221 g), ethanol (150 ml) and phosphoric acid 0.1 M (5 ml) (variation of the recipe given by Zweig[12]). Naphthoresorcinol is a reagent especially used to reveal sugars and uronic acid.[13]

In combination 2, the silica gel 60 plate was impregnated with a solution of NaH_2PO_4 0.3 M for 30 minutes prior to the sample deposit (Prosek, in Sherma & Fried[11]). This plate was developed with the mixture *n*-butanol/ethanol/phosphoric acid 0.1 M (1:10:5). Visualization was done by spraying a solution of *p*-anisidine hydrochloride (4-methoxybenzene amine) 3% in *n*-butanol.[12]

The plates were dried with a hair dryer after the visualization step and the colored spots were revealed by heating the plates at 105°C for 15 to 20 minutes. Observation of the color of the spots was done in visible light and un-

der UV at 366 nm. Migration distances of the compounds were noted and hRf was calculated, according to the formula:

$$hRf = \frac{\text{distance moved by the solute}}{\text{distance moved by the mobile-phase front}}$$

Several TLC plates were necessary for all the reference compounds and several attempts were made to obtain a good resolution of the chromatograms (right concentration of the compounds). Table 1 lists the reference compounds used for the TLC.

FTIR analyses of the degradation compounds

Samples were ground with KBr pellets. Sample pellets were analyzed in the transmittance mode. A Perkin Elmer 1750 FTIR spectrometer was used.

In order to separate the organic part (less polar) from the hydrophilic part (sugars) in the brown line extract, partition using ethyl acetate and water (aqueous brown line extract) was carried out. The two phases were allowed to stand over 65 hours and were further separated and dried under vacuum over P_2O_5. Dry residues were analyzed by FTIR.

GC/MS analyses of the degradation compounds

Two analyses were carried out on two aqueous samples with a Hewlett-Packard GC 428 coupled to a (VG 70-Se) MS. The GC column used was 25 m × 0.25 mm Chrompack CP Sil 5 CB, He carrier gas. Elution times were respectively 30 minutes (separation of lower-molecular-weight compounds) and 41 minutes (separation of higher-molecular-weight compounds). A derivatization treatment of the samples was carried out to convert any polar -OH group (non-volatile) to non-polar ones (volatile) so that the sample could be analyzed in the GC. The derivatization, transformation of alcohol groups to trimethylsylil ether groups ($-OSi(CH_3)_3$) was carried out in the following manner. Extracts were freeze-dried and trimethylsylilated with the derivation reagents at 50°C for 30 minutes. Each sample was injected separately. The molecular weight (MW) of the compound or that of its trimethylsylilated derivative were obtained.

Results and Discussion

Brown degradation product extracts obtained

The colour of the aqueous extracts of brown lines ranged from yellow to brown, depending on the number of samples extracted. The pH of this aqueous extract determined with a pH meter was 4.5. The dried extracts

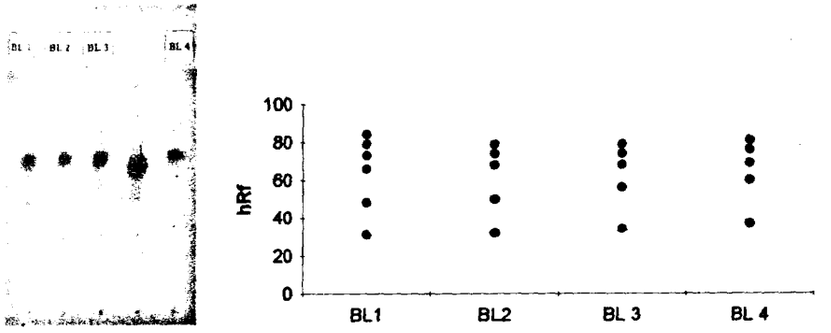


Fig. 3. **a**. Photograph of TLC of 4 brown line extracts – combination of development and visualization 1. **b**.Graphic presentation.

were a very dark brown viscous matter and had a caramel smell. The weight of the dry extracts ranged from 3 to 7 mg for 10 to 15 mildly intense brown lines extracted.

TLC of the degradation compounds

TLC is used as a routine analysis to identify complex mixtures of carbohydrates, for instance in the food industry. It is a simple method, relatively fast, sensitive and in many cases needs no special pretreatment of the samples. TLC is very useful to analyze the thermally unstable carbohydrates[14–18] and oligo- and polysaccharides that are not volatile enough to be directly analyzed by gas chromatography. It also has been used for the analysis of degradation products in paper.[19] Reference compounds were chosen because previous studies have identified them as compounds produced by the oxidation of cellulose,[20] by the oxidation of glucose,[20,21] by acid-catalysed dehydration of glucose,[16,22] by the treatment of D-glucuronic acid in slightly acidic aqueous solutions[15] and by the thermolysis of hydroxymethylfurfural.[23]

A thin layer chromatogram of 4 brown line extracts obtained with combination 1 is shown in Fig. 3. Table 2 gives the specifications of each spot obtained with combination 1 (Fig. 3) and Table 3 the specifications of each spot obtained with combination 2. The compounds identified in the brown line extracts as compared with the reference compounds in Table 1 are presented in Table 4. TLC appears to be a good technique for separation of the brown degradation products since it was possible to separate 5 spots (in the medium concentration deposits) to 6 spots (in the high concentration deposits) using combination 1. The drawback is that TLC requires numerous reference compounds: only 2 spots out of the 5/6 revealed with the combination 1 and 1 spot out of 2 revealed with the combination 2 could be identified.

Table 1. Reference compounds of the brown degradation compounds for TLC

Sugars	
aldohexoses:	D-glucose[a]
	D-galactose[b]
	D-mannose[a]
ketohexose:	D-fructose[b]
methylpentoses:	L-fucose (=6-deoxy-L-galactose)[a]
	L-rhamnose (=6-deoxy-L-mannose)[b]
aldopentoses:	D-arabinose[b]
	D-xylose[b]
disaccharide:	cellobiose[c]
non-cyclic polyols:	glycerol (1,2,3-propanetriol)[a]
	i-erythritol (1,2,3,4-butanetetrol)[a]
phenolic compound:	1,2,4-benzenetriol[c]
Other carbohydrates	
uronic acids:	D-glucuronic acid[a]
	D-gluconic acid[a]
	D-glyceric acid[a]
	glycolic acid[a]
	saccharic acid (=D-glucaric acid)[a]
uronic acid lactones:	D-glucuronic acid γ-lactone[a]
	D-gluconic acid δ-lactone[a]
	D-saccharic acid 1,4-lactone[a]
furan derivatives and other organic acids:	2-furoic acid[c]
	2,3-dihydroxybenzoic acid[c]
	levulinic acid (=4-oxopentanoic acid)[c]
	5-(hydroxymethyl)-2-furan carboxylic acid[c]
	2,5-furan dicarboxylic acid[c]
	furfural (2-furaldehyde)[c]
	hydroxymethylfurfural (HMF, hydroxymethyl-2-furaldehyde)[c]

[a] Compounds obtained from Sigma Chemical Co.
[b] Sugars from the Centraal Laboratorium collection.
[c] Compounds graciously offered by the Department of Research on Carbohydrates of Delft University of Technology (the Netherlands).

FTIR analyses of the degradation compounds[a]

IR provides indications on the nature of the organic groups present. To elucidate the complete structure of an organic compound, especially a mixture of different compounds as the brown line extract, IR spectroscopy usually is used in addition to other analyzing techniques. FTIR already has been used

[a] The table of organic functions characteristic band assignments from Silverstein[25] and from Conley.[26]

Table 2. Specification of the spots of different brown line extracts separated in TLC with the combination of development and visualization 1

Observation		hRf (migration)			
Visible	UV	BL1	BL2	BL3	BL4
a-brown (slight)	–	31	32	34	37
b-bluish (slight)	blue	48	50	56	60
c-blue	violet-blue	66	68	68	69
d-bright orange	white	73	74	74	76
e-gray-brown	reddish	79	79	79	81
f-brown (slight)	whitish	84	–	–	–

Table 3. Specifications of the spots of a brown line extract separated in TLC with the combination of development and visualization 2

Observation		hRf
Visible	UV	BL
a′-yellow	orange	47
b′-brown	brown	70

Table 4. Compounds present in brown line extracts as compared with reference compounds

	Compounds detected	Combination of development and visualization used
Sugars	D-glucose	1 ⎫
	D-arabinose	1 ⎬ (spot c)[a]
	D-galactose	1 ⎭
		1 (spot b)
Uronic acids and lactones	D-glururonic acid	1 (spots b or c) and 2 (spot a′)
	D-gluconic acid	1 (spot c)
	D-gluconic acid δ-lactone	1 (minor component)

[a] Spot c seems to represent a mixture of compounds of similar hRf and coloration with naphthoresorcinol.

to characterize the composition of papers[19] and to study the photo-oxidation of cotton cellulose.[24] Fig. 4 shows the IR spectrum of the total dry extract of degradation products. It is the result of the subtraction of the IR spectrum of a dry extract of clean Whatman paper no. 5 with no brown line from the IR spectrum of the dry extract of the brown lines (i.e., subtraction of any ab-

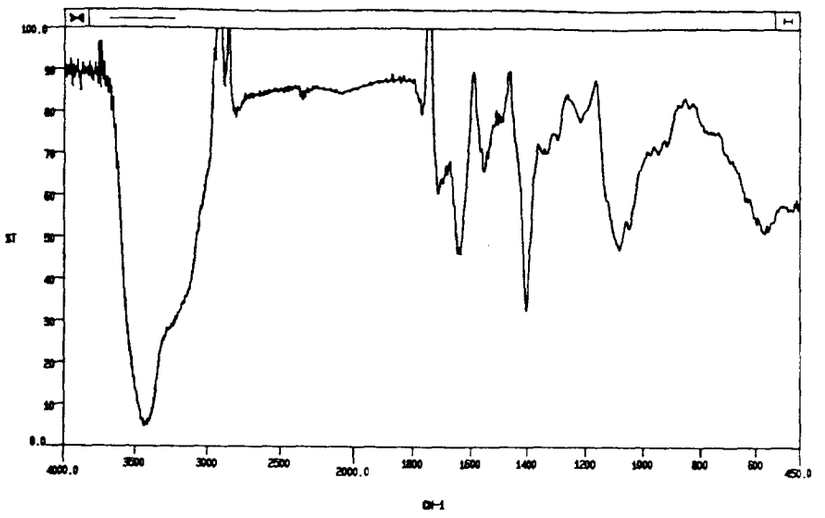


Fig. 4. IR spectrum of the total dry residue of the extract of brown degradation products.

sorption band from cellulose). Table 5 lists the major bands from this dry extract and the bands assignments. Organic groups likely to be present in the brown extract are alcohol (as expected for cellulose derivatives), carbonyl (probably from ketones or lactones), ethylenic and ether. No evidence of the presence of carboxylic acids is found since the characteristic bands of the stretching vibration frequency of acidic O-H (ν_s O-H) around 2700-2500 cm^{-1} are absent. However, it is more likely that carboxylic ions are present. Fig. 5 shows the IR spectrum of the dry residue from the aqueous phase of the partition ethyl acetate/aqueous extract of degradation products (any absorption band from cellulose is subtracted). The colored compounds stayed in the aqueous phase while the organic phase remain uncolored. Table 6 shows the band assignments. Except for the absence of bands attributed to ethylenic links, the functional groups likely to be present in this extract are the same as compared to the total dry extract shown in Fig 4. Here again, the absence of absorption bands from acid function is noted. Fig. 6 is the IR spectrum of the dry residue of the organic phase of the partition ethyl acetate/aqueous extract of degradation products (any absorption band from cellulose is subtracted). Band assignments can be found in Table 7. Functional groups likely to be present are carbonyl groups (maybe aldehyde, ketone, ester or lactone), ether groups and aromatic ring compounds. The presence of ethylenic links could explain the color formation since browning is produced by the presence of unsaturated compounds with conjugated double

Table 5. Interpretation of IR spectrum of the total dry extract (Fig. 4).

Organic groups	Vibration frequency (v) (cm^{-1})	Vibration type	Comments
Alcohol	3400–3000 (broad)	ν_s O-H*	Normally around 3700–3500 but can be shifted to lower frequency if intermolecular H bonds are present. Probably polymers.
	1083	ν_s C-O	primary or secondary alcohol
	1402	ν_b O-H*	
Carbonyl	1768	ν_s C=O	Probably from a ketone or a lactone (since ν_s C-H of an aldehyde does not appear in the area 2880–2650). Normally appearing around 1740–1700, but could be shifted because of the conjugation with an aromatic ring structure of 5 or 6 carbons.
	near 1100	ν_b C-C-C and ν_s C-C of C-C=O | C	ketone
Ether	1150–1060	ν_s C-O-C	aliphatic ether
Carboxylic ions	1640	ν_s COO^- assymmetric	
	1768 and 1700 (small)	ν_s C=O	
	1402	ν_s COO^- symmetric	
Ethylenic C=C	3400–3000 (broad)	ν_s=C-H	
	1640	ν_s C=C	
	1000–800 (small)	ν_b=C-H	

ν_s=stretching vibration frequency
ν_b=bending vibration frequency

bonds. No evidence of alcohol or acid groups was found. It was surprising that no IR spectrum showed an acid group absorption band, when methylene blue dyeing as well as TLC positively identified the presence of acidic components. However, like Fox[7,8] we found that vibration frequencies of carboxylic ions were possibly present. Carboxylic acids could ionize in the aqueous medium and only be detectable in the IR spectra as their salts. The partition experiment between the aqueous phase and the organic phase led to a good separation of the mixture compounds: spectra of Fig. 5 and 6 have a

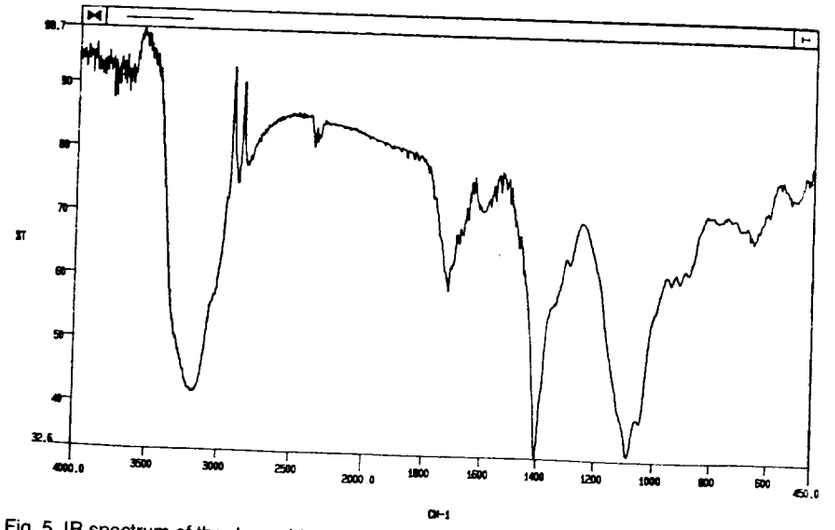


Fig. 5. IR spectrum of the dry residue of the aqueous phase of the partition ethyl acetate/aqueous extract of brown degradation products.

good resolution and are clearly different. The brown line extract includes polar compounds as the alcohols which stay in the aqueous phase, and less polar compounds, probably as aromatics or unsaturated compounds found

Table 6. Interpretation of IR spectrum of the dry extract of the aqueous phase of partition (Fig. 5).

Organic groups	Vibration frequency (v) (cm^{-1})	Vibration type	Comments
Alcohol	3400–3000 (broad)	ν_s O-H*	Same bands as spectrum in Fig. 4. See comments Table 5
	1083	ν_s C-O	Primary or secondary alcohol
	1402	ν_bO-H*	
Carbonyl	1720	ν_s C=O	Probably from a ketone (see comment on carbonyl band in Table 5)
Carboxylic ions	1768	ν_s C=O	
	1402	ν_s COO^- symmetric	

ν_s=stretching vibration frequency
ν_b=bending vibration frequency

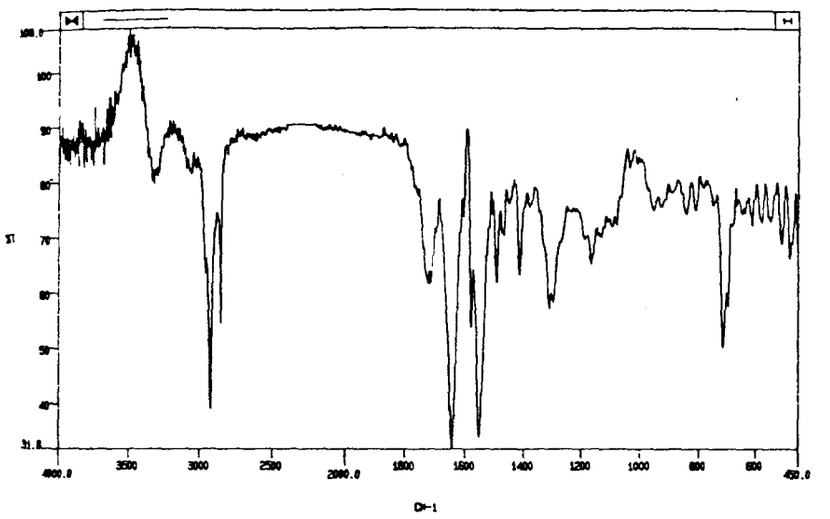


Fig. 6. IR spectrum of the dry residue of the organic phase of the partition ethyl acetate/aqueous extract of brown degradation products

in the organic phase. The carbonyl-containing compounds (ketones or aldehydes), lactones and other mildly polar compounds with ether linkages appear to be equally divided in the two phases.

GC/MS analyses of the degradation compounds

The peaks obtained on the chromatograms correspond to the MW of the compounds separated. The chromatogram obtained in 30 minutes of elution time showed peaks ranging from 97 to 744. The chromatogram obtained in 41 minutes of elution time showed peaks ranging from 234 to 1210. The compounds identified in the brown line extract are listed in Table 8. The identification was based on the comparison of the MW and the complete mass spectrum of each peak with the complete mass spectra of organic compounds from a data base of carbohydrates. Compounds identified were: galactose, arabinose, cellobiose, gluconic acid δ-lactone. Peaks probably corresponding to monosaccharides (C_4, C_5 and C_6), small oxidized fragments or less polar compounds and disaccharides with or without oxidation groups attached were also present. Unfortunately, all the peaks could not be identified. This could be due to an incomplete derivatization process. The values of MW of the brown line compounds would be different from those of the same theoretical trimethylsylilated compounds and therefore not identified by the data

Table 7. Interpretation of IR spectrum of the dry extract of the organic (ethyl acetate) phase of partition (Fig. 6).

Organic groups	Vibration frequency (v) (cm^{-1})	Vibration type	Comments
Carbonyl: aldehyde, ketone, ester or lactone	1725–1715 (doublet)	ν_s C=O*	One is from an aldehyde, the other maybe from a ketone, an ester or a lactone (normally around 1740; α, β-unsaturated ester around 1730–1715)
	2850	ν_s C-H	Aldehyde
	1310	ν_s C-O	Ester (normally around 1300–1100)
Ether	1163	ν_s C-O-C	
	890–830 (small)		Possibly peroxides
Aromatic	2900	ν_s C-H	Normally around 3100–3000
	1643+1550	ν_s C=C	Substituted aromatic ring (normally between 1610–1480)
	713	ν_b C-H*	

ν_s=stretching vibration frequency
ν_b=bending vibration frequency

Table 8. Possible compounds identified from the molecular weight peaks of the 2 gas chromatograms

Chromatogram showing lower MW compounds		Chromatogram showing higher MW compounds	
Peaks (MW)	Compound identification	Peaks (MW)	Compound identification
<300	C_4 sugars, or less polar compounds or small oxidized cleaved fragments	>700	Disaccharides with or without oxidized groups attached
374+376	Pentose: probably arabinopyranose	911	Probably cellobiose
473+504	Hexose: probably galactose	<700	Monosaccharides (C_6 and C_5), low MW or less polar oxidation compounds
>700	Disaccharides with or without oxidation groups	466	Probably gluconic acid δ-lactone

base. It would be necessary to inject each reference compound on the column in the same exact conditions used for the analysis of the mixture to be identified, in order to compare retention times and ensure a qualitative study. If retention times are close, a co-injection of the pure reference compound and the mixture would confirm the presence of the suspected compound when the 2 peaks superpose. This could not be done here but should be considered for future analyses. The two gas chromatograms showed a good separation of the compounds. Therefore, it can be expected that following the procedure described above, it would be possible to identify all the compounds of the mixture. A pre-purification of the brown line extract using gel filtration or grafted silica phases could help to provide a better analysis. However, a much larger amount of sample will be required for these techniques since they involve a significant dilution effect and loss of material.

General discussion

All of the analysis techniques tested successfully separated the brown line mixture compounds. It would be interesting to combine the separation techniques in order to have a better identification. TLC could be carried out as a first step in the separation (avoiding the visualization treatment which changes the structure of the compounds). The spots recovered from the solid phase could be injected separately after derivatization, in the GC/MS. High-performance liquid chromatography (HPLC) would also be a suitable technique since it is commonly used for the identification of sugars and does not require derivatization of the polar compounds. Initial attempts in using HPLC did not give satisfactory resolution, although the presence of glucuronic acid was indicated. The brown line extract could be hydrolyzed prior to the analysis: a complete hydrolysis, cleaving all of the glycosidic linkages of the disaccharides or oligosaccharides of the extract would exclusively lead to monomeric units: monosaccharides or oxidized residues from a glucose unit. The chromatogram should show a restricted number of peaks and would be more easily interpretable. Moreover, depending on the monomeric units obtained, it would be easy to establish where oxidation took place on the glucose residues. The compounds identified in the extract of degradation products and, in general, the numerous compounds present seem to indicate that the oxidation at the wet/dry interface produces the detachment of small cleaved fragments and occurs randomly on the glucose residue, forming numerous low-molecular-weight degradation products, which could additionally be further oxidized. Oxidation also occurs randomly along the cellulose chain without cleavage since after the extraction of the brown products from the paper, oxidized groups still were present along the macromolecule.[1]

The formulae of the compounds identified in the brown line extracts are presented in Fig. 7. The presence of glucose in the mixture seems to indicate the action of acidic hydrolysis of the glycoside link (as previously indicated, the pH of the extract is 4.5), or a peeling-off reaction by Isbell's β–alkoxy carbonyl elimination (although this reaction normally occurs at al-

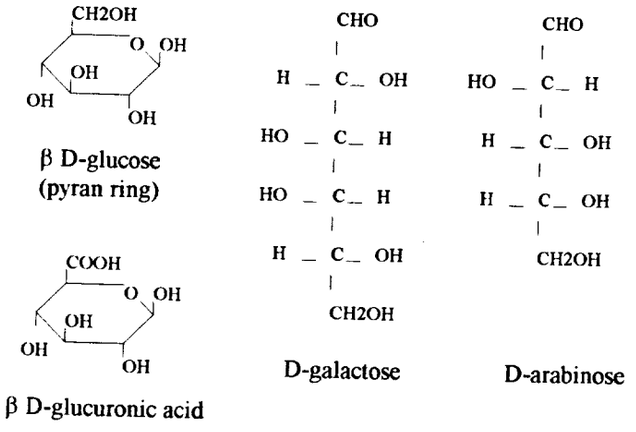
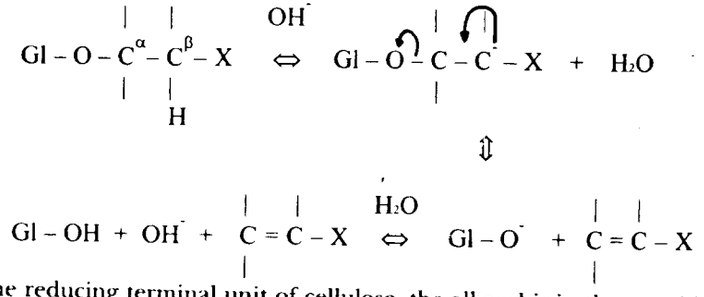


Fig. 7. Formulae of the compounds identified.

kaline pH). The alkaline degradation of cellulose from the reducing end is explained according to Isbell's theory of β-elimination, by which he proposed to explain the instability towards alkalis of glycosides of alcohols containing electronegative groups in the β-position (Isbell, in Golova et al.[27]). An alkoxy group should be present in the β-position relative to the aldehyde group to obtain the elimination:



In the reducing terminal unit of cellulose, the alkoxyl is in the γ-position to the aldehyde group. Detachment of the reducing terminal glucose unit will become possible after isomerisation into a fructose unit.

According to Lewin et al.,[28–30] the reaction sequence leading to the formation of the colored substances in cellulose seems to involve the presence of active aldehyde groups formed by oxidation of the terminal anhydroglucose unit. The next step is the peeling-off of glucose units from the new reducing chain ends, formed by the cleavage of the oxidized unit. The peeled glucose units undergo isomerization and fragmentation. The fragments formed undergo condensation to furan derivatives and to carbonyl-containing colored compounds. Active aldehyde groups leading to this peeling-off reaction should be on C6 (leading to a cleavage on C4), on C2 (followed by a cleavage of the linkage C1-C2), or on C1 with the presence of a carboxyl on C6. A ketone on C2 or on C4, or a carboxyl on the C6 also lead to peeling-off.

The presence of cellobiose indicates a cleavage of the glycoside link. Gluconic acid, which forms readily its lactone, evidences acidic oxidation on C1 of the terminal glucose unit followed by the cleavage of the chain (or vice versa). Glucuronic acid evidences acidic oxidation on the C6 of the terminal glucose unit followed by the cleavage (the -COOH group sensitizes the neighboring glycosidic link to cleavage). Arabinose could indicate a dehydrogenation of the sugar on the C6, or a Ruff degradation of the gluconic acid. Ruff degradation is the decarboxylation of an aldonic acid during oxidation with hydroperoxide radicals.

No isomerization of glucose to other C_6 sugars is clearly evidenced, although the gas chromatograms indicated the presence of several C_6 sugars. According to Lewin et al.,[30] a fragmentation of the glucose could form additional compounds, not identified here, as hydroxyacetone or glyceraldehyde. The latter is a precursor of colored furan derivatives, by condensation with another glyceraldehyde or with different fragmentation compounds. Furfural, HMF, and other colored degradation compounds from dehydration of sugars in acidic medium were not detected here.

Conclusion

Several degradation compounds present in the brown lines formed at a wet/dry interface on cellulose have been identified. These include monosaccharides as D-glucose, D-arabinose, D-galactose, disaccharides as cellobiose and uronic acids as D-glucuronic acid, D-gluconic acid and its δ-lactone. Other compounds formed from oxidation and cleavage of fragments from the cellulose chain and other disaccharides with and without oxidized groups attached are present in the brown line but could not be identified. In order to identify all the degradation products of the cellulose at the wet/dry interface, a number of analytical techniques were attempted and were found to be potentially useful. To that effect, this work represents a basis for future research. The improvement of the usefulness of these techniques to the analy-

sis of brown line products was discussed. A number of problems were encountered, the major one being quantification of degradation products in samples. The procedure of extraction led to some loss of material, and it was very time-consuming to collect a significant amount of extracted material for analysis. In the future, it would be necessary to set up a more efficient procedure to create or simulate the wet/dry interface. The use of microcrystalline cellulose from which water could evaporate is one alternative. It must be verified that the degradation resulting from alternate sample preparation methods is identical.

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The author would like to acknowledge the Centraal Laboratorium voor Onderzoek van Voorwerpen van Kunst en Wetenschap, where this work has been carried out, and particularly Dr J. Hofenk de Graaff and Dr J. Neevel. Grateful acknowledgement also to the Delft University of Technology where GC/MS analyses were done, and especially Dr. A. Abbadi for technical support and helpful suggestions. Thank you also to S. Tse and L. Selwyn from the Canadian Conversation Institute for helpful comments during the preparation of the manuscript. The author was supported by the Rotary Foundation International.

SUMMARIES

Degradation of cellulose at the wet/dry interface. II. An approach to the identification of the oxidation compounds

Results from a study of the degradation products formed by the oxidation at the wet/dry interface of pure cellulose Whatman filter paper no. 5 are presented. Analysis techniques were thin layer chromatography (TLC) Fourier transform infrared spectroscopy (FTIR) and gas chromatography coupled to mass spectrometry (GC/MS). Their advantages and drawbacks in identifying the degradation compounds of the wet/dry interface are discussed. IR spectra showed the presence of carbonyl groups from aldehydes and ketones of polar and mildly polar compounds and the presence of ethylenic links of less polar compounds. The presence of conjugated systems could explain the brown color observed. TLC and GC/MS could identify sugars and uronic acids in the degradation products extracted from the cellulose. Their formation from the cellulose chain is explained.

Dégradation de la cellulose à l'interface humide/sec. II. Une approche dans l'identification des produits d'oxydation

Le présent article expose les résultats d'une étude sur les produits de dégradation formés par oxydation à l'interface humide/sec sur du papier Whatman no. 5, pure cellulose. Les techniques d'analyse utilisées pour l'identification des produits de dégradation sont la chromatographie sur couche mince (CCM), la spectroscopie infrarouge à transformée de Fomurier (IRTF) et la chromatographie en phase gazeuse couplée en spectrométrie de masse (CG/SM). Leurs avantages et inconvénients pour l'application à cette étude sont discutés. Les spectres IR ont montré la présence de groupements carbonyles (aldéhydes et cétones) appartenant à des composés polaires ou moyennement polaires, ainsi que la présence de doubles liaisons appartenant à des composés moins polaires. La présence de doubles liaisons conjuguées pourrait expliquer la coloration brune de l'extrait des produits de degradation. La CCM et la CG/SM ont permis d'identifier dans les produits de dégradation extraits de la cellulose differents sucres et acides uroniques. Une explication pour la formation de ces composés à partir de la macromolécule de cellulose est avancée.

Der Abbau von Cellulose an der Übergangsstelle Naß/Trocken. II. Ein Versuch zur Identifizierung der Oxidationsprodukte

Es werden die Ergebnisse einer Untersuchung vorgelegt, die den Produkten galt, die durch Oxidation an der Übergangsstelle Naß/Trocken in Papier aus reiner Cellulose (Whatman Nr. 5) entstanden waren. Die Analysemethoden waren: Dünnschichtchromatographie, Infrarotspektroskopie nach Fourier und Gaschromatographie in Verbindung mit Massenspektrometrie. Es werden die Vor- und Nachteile der verschiedenen Analysemethoden diskutiert. Infrarotspektren zeigen das Vorhandensein von Carbonylgruppen in Aldehyden und Ketonen in polaren und leicht polaren Substanzen sowie von Doppelbindungen in gering polaren Substanzen an. Die letzteren können die braune Farbe in den Abbauprodukten erklären. Die chromatographischen Methoden erweisen das Vorhandensein verschiedener Zucker und Uronsäuren in den Abbauprodukten. Es wird erklärt, wie aus dem Cellulose-Kettenmolekül entstehen können.

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The Degradation of Cellulose with Ferric and Cupric Ions in a Low-acid Medium

by MARINA BICCHIERI & SABRINA PEPA

Degradation of Cellulose

The cellulose polymer chain can be degraded mainly by hydrolytic or by oxidative mechanisms. Hydrolysis can occur both in acid and in alkaline media[1-6] and the most important effect is a depolymerization of the cellulose chain, due to the attack to the β-glucosidic bond. Alkaline hydrolysis takes place only at high temperatures and with strong alkalis, but it plays a very important role if cellulose contains oxidized groups. In this case, when β-alkoxy-carbonyl groups are present in the molecule, the alkaline hydrolysis occurs at lower temperatures, even with diluted alkalis, and it can become the chief degradative mechanism, especially if the cellulose is submitted to a strong deacidification.

The carbonyl groups can be located (Fig. 1) on C6; C2 (or C3); both on C2 and C3, and after cleavage of the C2-C3 bond, there are two possible sites for the aldehyde group on C2 and C3.

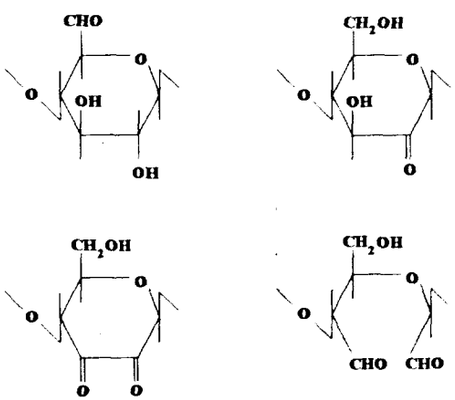

Fig. 1. Sites of oxidation in the cellulose ring

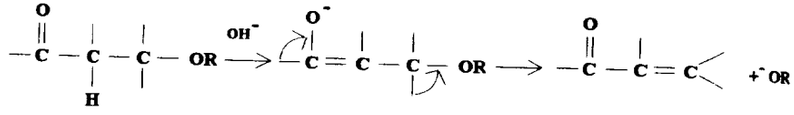

Fig. 2. β-alkoxy-elimination mechanism

In an alkaline medium a β-alkoxy elimination occurs and the general scheme that leads to cellulose chain depolymerization is reported in Fig. 2.

Metallic cations too play an important role in cellulose degradation[7,8]. Some authors[9] propose a free radical mechanism for the cellulose-metal interaction (Fig. 3) in which the metal acts as a catalyst in the homolytic scission of the cellulose peroxide (Fig. 4). It seems that the extraction of the hydrogen ion occurs prevalently at the C1 position, where a peroxy radical is then formed.

Other authors[10] postulate a Lewis mechanism that involves either the semiacetalic oxygen on the anhydroglucose unit or the β-glucosidic oxygen (Fig. 5) with formation of donor-acceptor bonds. In the first case a cleavage

Initiator

$$I \rightarrow I^{\cdot}$$
$$I^{\cdot} + O_2 \rightarrow IOO^{\cdot}$$
$$CELLH + I^{\cdot} \rightarrow CELL^{\cdot} + IH$$
$$CELLH + IOO^{\cdot} \rightarrow CELL^{\cdot} + IOOH$$
$$CELLH + O_2 \rightarrow CELL^{\cdot} + HOO^{\cdot}$$

Propagation

$$CELL^{\cdot} + O_2 \rightarrow CELLOO^{\cdot}$$
$$CELLOO^{\cdot} + CELLH \rightarrow CELLOOH + CELL^{\cdot}$$

Products formation

$$CELLOOH \rightarrow CELLO^{\cdot} \text{ or } CELLOO^{\cdot}$$
$$CELLO^{\cdot} \text{ or } CELLOO^{\cdot} \rightarrow PRODUCTS$$
$$CELLOOH \rightarrow PRODUCTS$$

Fig. 3. Free radical mechanism for the formation of cellulose peroxide

$$CELLOOH + M^{n+} \rightarrow CELLOO^{\cdot} + H^{+} + M^{(n-1)+}$$
$$CELLOOH + M^{(n-1)+} \rightarrow CELLO^{\cdot} + OH^{-} + M^{n+}$$

Fig. 4. Metallic catalysis following the cellulose peroxide formation

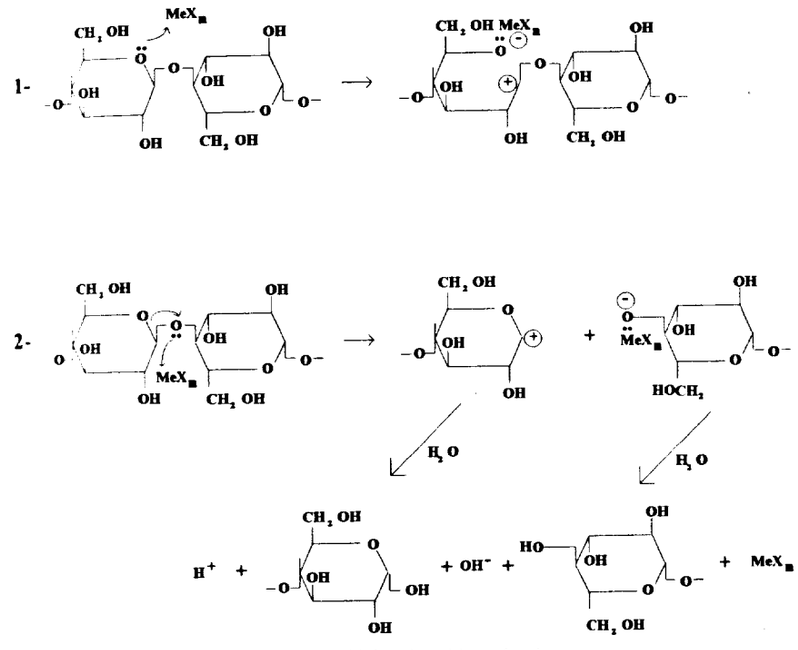

Fig. 5. Metallic degradation of cellulose with Lewis acid mechanism

of a glucopyranose unit occurs that can be easily attacked by other degradative agents. In the second mechanism a depolymerization of the chain takes place immediately.

The first aim of our experimental work is to quantify the degradative effects induced by iron and copper ions in a low-acid medium, to verify whether both cations produce the same deterioration and whether experimental data are in agreement with one of the mechanisms proposed in the literature.

The second goal is to determine whether the use of a reducing material can obstacle the oxidation catalyzed by metals and at the same time whether the treatment produces an optical bleaching of paper.

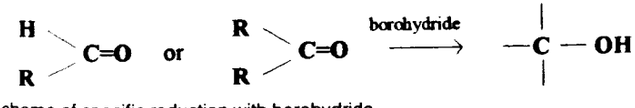

Fig. 6. Scheme of specific reduction with borohydride

As a reducing agent it is possible to use borohydrides[11], which specifically react with two types of carbonyls, aldehydes and ketones, reducing them back to alcohol (Fig. 6).

Several investigations[12–16] on tetramethylammoniun, tetraethylammoniun and sodium borohydrides have been reported in the literature, but the use of these products did not show a large increment of the degree of polymerization, moreover, sodium borohydride solutions seem to have too high a pH value to permit their use for restoration purposes. The high alkaline ambient in fact allows the β-alkoxy elimination and it has also been demonstrated that high concentration of sodium ions can induce hydrolysis.

For these reasons we decided to investigate other reducing compounds. Sodium cyanoborohydrure and borane tert-butylamine complex gave good results[17]. The first compound is weaker than sodium borohydride and is an extremely selective reagent in reducing aldehydes and ketones, but only in an acid-buffered solution (pH 3–4). Due to its toxicology and to the need of its application in acid medium, it is unsuitable for restoration. The borane tert-butylamine complex has a reactivity quite different to that of diborane (for example, acids are not reduced) and is similar to sodium borohydride, except for its reaction with carbon-carbon double bonds (this group is not reduced by sodium borohydride). It is soluble in water and in organic solvents, like toluene, and it is then a very versatile reducing agent.

Experimental Set-up

Materials

- Whatman paper no. 1 for chromatography
- Aqueous solution of iron III chloride $5 \cdot 10^{-3}$ M
- Aqueous solution of copper II chloride $5 \cdot 10^{-3}$ M
- Aqueous solution of borane tert-butylamine complex $2 \cdot 10^{-1}$ M

Ageing

Untreated and treated samples were aged as follows:
- method ISO 5630/3-1981: 80°C, 65% RH
- total time 28 days; drawing at 0, 7, 14, 21, 28 days

Measurements

On untreated and treated samples, before and after each time of ageing, the following were performed:
- pH of aqueous extract, hot extraction method (TAPPI T435 om-88)
- blue reflectance factor (ISO 2470/77)

- carboxyl content of cellulose (ASTM 1926-89)
- intrinsic viscosity of cellulose (modified ASTM 1795-90)
- moisture content of cellulose (ASTM 1348-89)

All values of experimental data are corrected by the moisture content (ASTM D1348-89). Measurements have been carried out on samples after conditioning at 23°C and 50% RH (ASTM D685-87).

Preparation of samples

The specimens were immersed in solutions of metals (ratio: 100 ml of solution/1 g of paper) for 15 min, then subjected to accelerated ageing. For the reduction, unaged and aged samples (treated and not with metal cations) were immersed in the reducing solution (ratio: 100 ml solution/1 g paper) for 5 hours.

Results

pH

pH was measured in accordance with TAPPI T435 om-88, using fresh boiled water distilled twice and carbon-dioxide-free.

The results, listed in Table 1 and presented in Fig. 7, show that both cations, especially iron, led to an acidification of the paper.

Table 1. pH as a function of ageing time
(TQ=untreated, Fe=treated with $FeCl_3$, Cu=treated with $CuCl_2$)

Time / Sample	0 days	7 days	14 days	21 days	28 days
TQ	6.58±0.02	6.40±0.02	6.21±0.02	6.04±0.02	6.02±0.02
Fe	5.99±0.02	5.95±0.02	5.60±0.02	4.99±0.02	4.58±0.02
Cu	6.39±0.02	6.33±0.02	5.90±0.02	5.99±0.02	5.50±0.02

Table 2. Diffuse blue reflectance factor (IRB%) as a function of ageing time
(TQ=untreated, Fe=treated with $FeCl_3$, Cu=treated with $CuCl_2$)

Time / Sample	0 days [%]	7 days [%]	14 days [%]	21 days [%]	28 days [%]
TQ	88.20±1.64	83.91±0.26	83.83±0.41	83.76±0.91	83.12±0.93
Fe	82.55±1.18	75.06±1.02	73.21±1.64	67.47±1.51	23.98±1.53
Cu	90.34±0.85	83.59±0.50	81.69±1.00	78.52±1.43	66.24±1.63

Fig. 7. pH as a function of ageing time

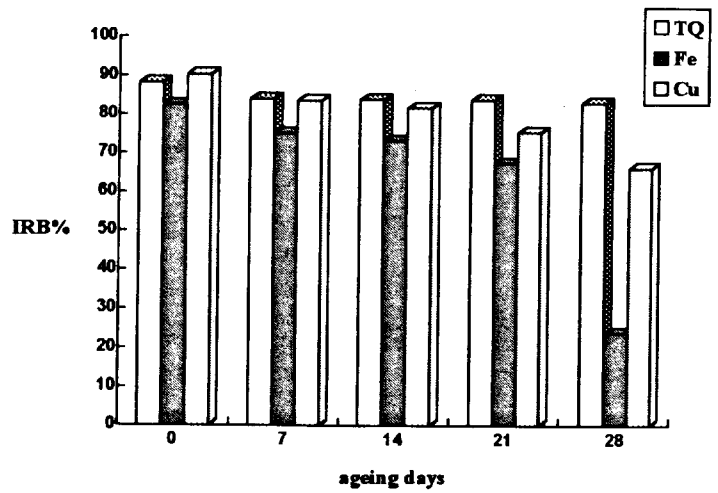

Fig. 8. Diffuse blue reflectance factor (IRB%) as a function of ageing time

Brightness

Diffuse blue reflectance factor (IRB%) measurements are listed in Table 2 and presented in Fig. 8. We can see that iron ions immediately induce a yellowing of paper, deeper than copper.

Table 3. Millimoles of carboxyl as a function of ageing time and treatment.
(TQ=untreated, Fe=treated with $FeCl_3$, Cu=treated with $CuCl_2$)

Time [days]	COOH TQ [millimoles]	COOH Fe [millimoles]	COOH Cu [millimoles]
0	$0.3306\pm2.65 \cdot 10^{-3}$	$0.3984\pm3.98 \cdot 10^{-3}$	$0.5171\pm5.17 \cdot 10^{-3}$
7	$0.3559\pm2.88 \cdot 10^{-3}$	$0.4934\pm4.93 \cdot 10^{-3}$	$0.7303\pm7.30 \cdot 10^{-3}$
14	$0.4340\pm3.47 \cdot 10^{-3}$	$0.6689\pm6.69 \cdot 10^{-3}$	$0.7865\pm7.87 \cdot 10^{-3}$
21	$0.4721\pm3.78 \cdot 10^{-3}$	$0.7070\pm2.11 \cdot 10^{-2}$	$0.7900\pm2.20 \cdot 10^{-2}$
28	$0.4858\pm3.89 \cdot 10^{-3}$	$0.7471\pm2.20 \cdot 10^{-2}$	$0.7851\pm2.02 \cdot 10^{-2}$

Carboxyl content

The carboxyl content of cellulose is carried out in accordance with ASTM 1926-89, by measurement of absorbance at 620 nm of a methylene blue solution. The reaction between COOH groups and methylene blue consists in a cationic exchange:

(1) $RCOOH+MB^{+} \leftrightarrow RCOOMB+H^{+}$

where COOH=carboxyl groups in cellulose and MB^{+}=methylene blue

Equation (1) shows that absorbance is proportional to the ratio $[MB^{+}]/[H^{+}]$. To have a quantitative substitution of all carboxyl groups it is also necessary to operate in alkaline-buffered solution (pH 8–9). The increase of oxidized groups in cellulose molecules causes a decrease in methylene blue concentration, measured photometrically, which is a function of the ion-exchange capacity of cellulose. The results of measurements, reported as millimoles of carboxyl per 100 g of cellulose, are listed in Table 3 and presented in Fig. 11.

Intrinsic viscosity

The behavior $\log [(\eta_{rel}-1)/c]$ as a function of c, which can be represented by a straight line, has been studied for each ageing time and treatment. η_{rel} is

Table 4. [η] as a function of ageing time
(TQ=untreated, Fe=treated with $FeCl_3$, Cu=treated with $CuCl_2$)

Time / Sample	0 days	7 days	14 days	21 days	28 days
TQ	9.75±0.13	8.37±0.10	8.35±0.04	6.98±0.11	7.20±0.13
Fe	4.49±0.05	3.25±0.06	2.43±0.04	1.51±0.04	1.25±0.02
Cu	4.36±0.03	3.16±0.06	1.99±0.06	1.60±0.05	1.61±0.04

Table 5. Average degree of polymerization (DP^0) from viscosity measurements as a function of time ("cold" method). (TQ=untreated, Fe=treated with $FeCl_3$, Cu=treated with $CuCl_2$)

Time / Sample	0 days	7 days	14 days	21 days	28 days
TQ	1521±21	1305±16	1302±6	1090±17	1123±20
Fe	596±6	507±7	378±5	187±5	155±2
Cu	680±4	493±8	311±8	199±6	200±5

the relative viscosity of the solution of paper in cupriethylenediamine hydroxide, that is, the ratio between solution viscosity and solvent viscosity; c is the concentration of the cellulose solution in g/dl. Instead of obtaining the values of intrinsic viscosity [η] from listed tables (ASTM or AFNOR methods), we decided to construct the straight line and to calculate [η] by extrapolation at zero concentration. The straight-line parameters have been ob-

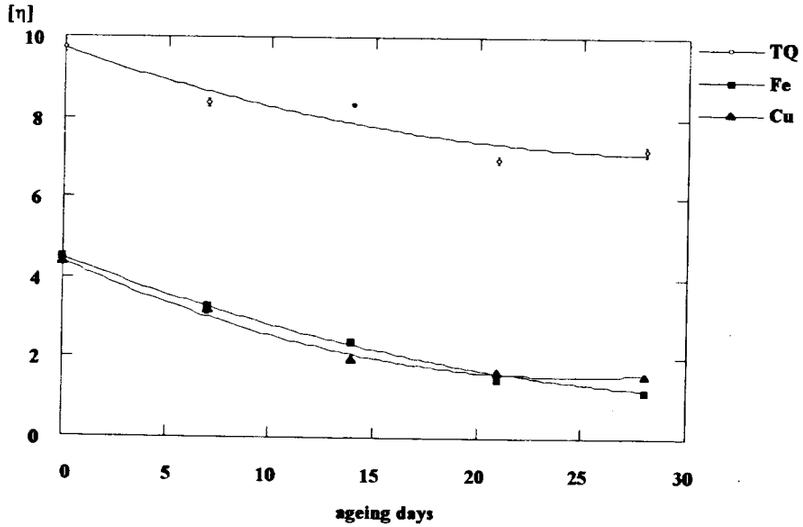

Fig. 9. [η] as a function of ageing time, where: y=[η]; x=t (days) $y=a+b \cdot e^{x/\tau}$

parameters	TQ	Fe	Cu
a	6.4197	0.8085	1.173
b	3.2854	3.7544	3.2394
τ	17.236	14.665	11.755

tained using a least-square-fit method, taking into account correctly, for each measurement, the proper error. The results are listed in Table 4 and presented in Fig. 9.

From Mark-Houwnik equations:

(2) $[\eta]=K\bar{M}_v^{\alpha}$

(3) $[\eta]=K'\bar{DP}_v^{\alpha}$

we can calculate the average viscosity degree of polymerization listed in Table 5.

Oxidation measurement

To evaluate the oxidation of the polymeric chain, we modified the viscosity method. We can induce the β-alkoxy elimination mechanism by heating at 60°C, under nitrogen and 1 hour, the solutions of paper in cupriethylenediamine hydroxide. This mechanism led to the cleavage of the glucosidic bond located in β compared with the group oxidized to aldehyde or ketone. The measured average degree of polymerization (DP^{00}) is lower than the unheated degree of polymerization (DP^0) in inverse proportion to the amount of cellulose oxidation. If: N_1=number of monomers (anhydroglucose unit); N_0=number of cellulose chains; S=number of scissions, we can write

$$(4)\quad DP^0 = \frac{N_1}{N_0} \qquad DP^{00} = \frac{N_1}{N_0 + S}$$

When we refer to 1000 glucosidic bonds, we have:

$$(5)\quad S‰ = 1000 \cdot \left(\frac{1}{DP^{00}} - \frac{1}{DP^0} \right)$$

The obtained values of (DP^{00})are listed in Table 6. Table 7 contains the calculated number of scissions out of 1000 glucosidic bonds.

Table 6. Average degree of polymerization (DP^{00}) of heated samples from viscosity measurements as a function of time ("hot" method).
(TQ=untreated, Fe=treated with $FeCl_3$, Cu=treated with $CuCl_2$)

Time / Sample	0 days	7 days	14 days	21 days	28 days
TQ	1335±13	1287±10	1247±8	1186±8	1103±9
Fe	329±5	387±7	322±6	182±2	140±3
Cu	635±7	494±8	182±3	192±4	193±3

Table 7. Scissions $^0/_{00}$ of glucosidic bond. Column "a" contains the fraction ($^0/_{00}$) of scissions calculated with respect to initial time (DP^0 at t=0); in column "b" the scissions are calculated for each ageing time interval (DP^0 is variable with the time).
(TQ=untreated, Fe=treated with FeCl3, Cu=treated with CuCl2)

Time	0 days	7 days		14 days		21 days		28 days	
Sample	a=b	a	b	a	b	a	b	a	b
TQ	0.09	0.12	0.01	0.15	0.034	0.19	0	0.25	0.016
Fe	1.37	0.91	0.61	1.28	0.461	3.81	0.150	4.77	0.691
Cu	0.10	0.56	0	4.02	2.280	0.18	0.183	3.71	0.181

Reduction amount measurement

Intrinsic viscosity measurements have to be carried out in alkaline medium; when in the polymeric chain there are oxidized sites, the solution in cuprietylenediamine favors the β-alkoxy elimination and causes an apparent decrease of the average polymerization degree. This decrease is not originated by ageing but it is due to the measurement method itself. The lowering of the polymerization degree is not evident for untreated paper, where the ageing effect is mainly due to hydrolysis, but is visible when metal cations are present, catalyzing oxidative reactions. In order to reduce this effect, which causes systematic errors, we carried out measurements of average polymerization degree, after reduction with borane tertbutylamine complex. The obtained values (from "cold" viscosity) do not suffer from systematic errors due to the β-alkoxy elimination and are closer to the true value of polymerization degree of paper. The results are listed in Table 8 and presented in Fig. 10.

Discussion

Experimental data show that iron and copper act differently in cellulose degradation. In the polymeric chain the sites, immediately permitting an oxidation to carboxyl, are located on C6, the only primary alcoholic group in the anhydroglucose unit. After the cleavage of 1-4-β-glucosidic bond and the

Table 8. DP^0 after reduction as afunction of ageing time.
(TQ=untreated, Fe=treated with $FeCl_3$, Cu=treated with $CuCl_2$)

Time	0 days	7 days	14 days	21 days	28 days
Sample					
TQ	1573±16	1481±10	1389±8	1297±8	1205±9
Fe	732±8	606±7	480±6	354±4	228±3
Cu	1200±10	987±8	774±3	561±4	349±3

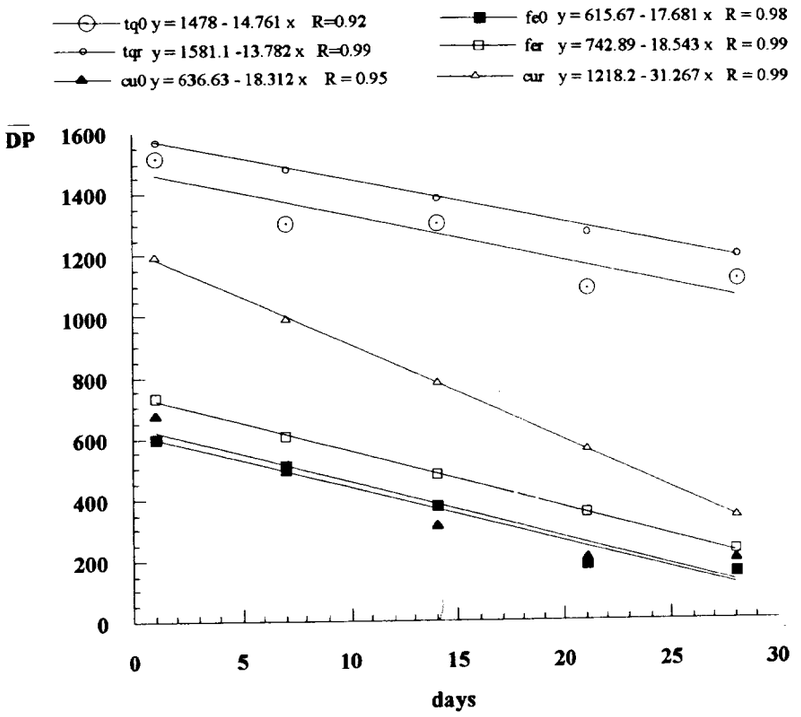

Fig. 10. Polymerization degrees (r=reduced; 0=not reduced)

subsequent equilibrium, in the terminal unit, between a cyclic and a linear structure, there is an increment of oxidizable sites. If the cleavage of C2-C3 bond occurs, two other carboxyl groups can form for each anhydroglucose unit. Fig. 11 shows that in papers untreated (TQ paper) and treated with iron (Fe paper), the formation of carboxyl groups follows the same law, different from the one that describes the behavior of papers treated with a copper solution (Cu paper).

Experimentally we find that the number of carboxyl is function of the time, accordingly to the following laws:

(6) $y=a+bx^2 \cdot e^{-x/\tau}$ for TQ and Fe papers
(7) $y=a-bx \cdot e^{-x/\tau}$ for Cu papers

where y=concentration of carboxyl groups [m moles/100 g of paper] and x=time [days].

We define N_0 as the number of carboxyl groups present in the paper at the initial time. This quantity is a function of the "history" of the paper: the pulping treatments, the time interval between the fabrication of paper and the chemical measurements, the storage conditions and so on. As a function of the time we can write:

(8) $N_{COOH}(t_0)=N_0$

(9) $N_{COOH}(t_0+\Delta t)=N_0+f(t)$

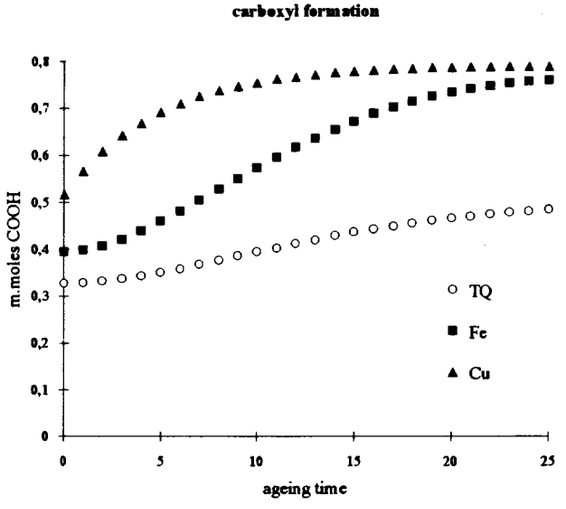

Fig. 11. Millimoles of carboxyl as function of ageing time and treatment, where y=millimoles COOH; x=time (days).
$y(TQ)=a+bx^2 \cdot e^{-(x/\tau)}$ R=0.997
$y(Fe)=a+bx^2 \cdot e^{-(x/\tau)}$ R=0.998
$y(Cu)=a-b \cdot e^{-(x/\tau)}$ R=0.999

parameters	TQ	Fe	Cu
a	0.32756	0.39499	0.79138
b	$1.2895 \cdot 10^{-3}$	$3.7443 \cdot 10^{-3}$	0.2747
τ	15.226	13.451	4.4998

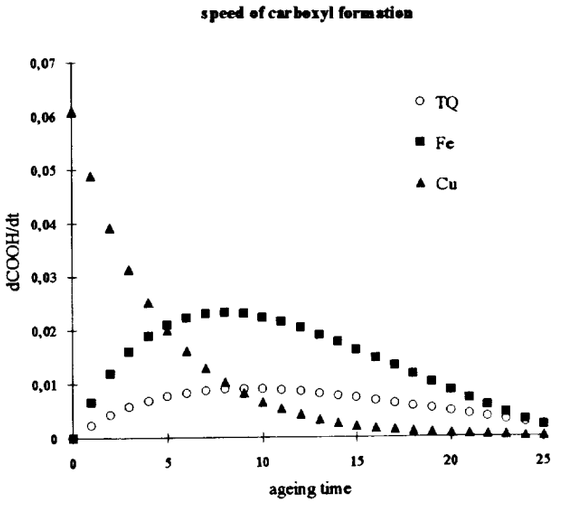

Fig. 12. Speed of carboxyl formation as a function of ageing time and treatment. y=speed =dCOOH(t)/dt; x=time (days).

From equations (6) and (7) we can derive the speed of carboxyl formation for TQ, Fe and Cu papers:

(10) $y'=2bx \cdot e^{-(x/\tau)} - \frac{bx^2}{\tau} \cdot e^{-(x/\tau)}$ for TQ and Fe papers

(11) $y'=\frac{bx}{\tau} \cdot e^{-(x/\tau)}$ for Cu papers

When neither the glucosidic bond nor the pyranosic ring breaks, the speed of carboxyl formation, bonded to C6, is a constant (0-4 days for Cu papers). When the oxidation of the primary alcoholic groups is coupled with the β-glucosidic bond cleavage, with subsequent oxidation, the speed of carboxyl formation (0-15 days for TQ and Fe papers) is a linear function of the time and then, when all possible sites have been oxidized, the speed of carboxyl formation decreases, following an exponential law. The speed of carboxyl groups formation as a function of ageing time (dN_{COOH} (t)/dt) is plotted in Fig. 12, showing that the saturation of sites progresses more rapidly for papers treated with copper ions than for papers untreated and treated with iron.

The observed behavior can be explained assuming that the interaction between metallic cations and cellulose involves different reactions: the iron seems to catalyze preferentially the cleavage of the 1-4-β-glucosidic bond (mechanism 2 in Fig. 5), accelerating the hydrolysis speed, while the cop-

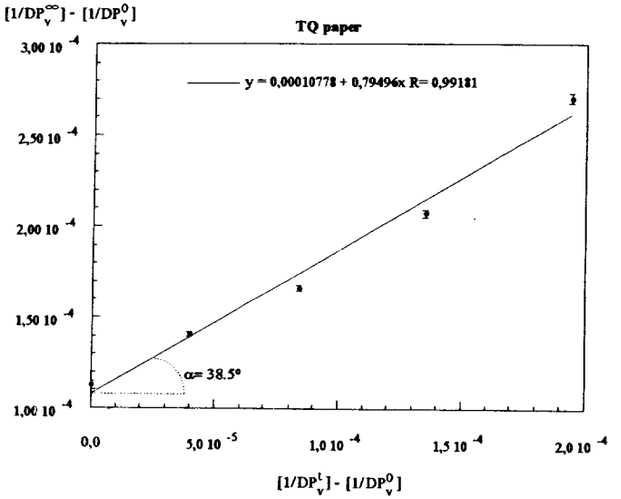

Fig. 13. Oxidative scissions vs total scissions for untreated papers

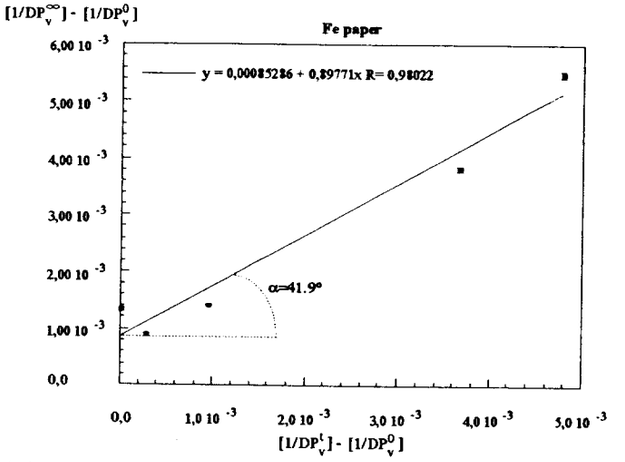

Fig. 14. Oxidative scissions vs total scissions for iron-treated papers

per acts especially on the glucopyranosic ring, opening it (mechanism 1 in Fig. 5), without changing the hydrolysis speed.

To confirm this interpretation, it is necessary to compare the data obtained for the average degrees of polymerization after and before reduction (Table 8 and Table 5).

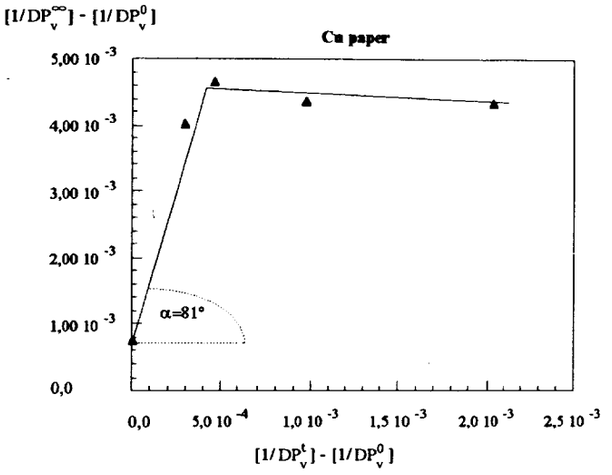

Fig. 15. Oxidative scissions vs total scissions for copper-treated papers

For the papers treated with copper, the values after reduction are two times higher than before the treatment. This behavior can be explained with the presence of oxidized groups in the pyranosic ring, which, allowing β-alkoxy elimination mechanisms, cause an apparent decrease of the chain length, before the reduction.

After the treatment with boranetert-butylamine complex, the carbonyl groups are reduced back to alcohol and the value of the degree of polymerization is higher than before, because the measurement is not affected by the presence of oxidized groups. For the papers treated with iron, the reduction does not cause a great increment of the degree of polymerization. The decrease in the cellulose chain length can indeed be explained as mainly due to the cleavage of the 1-4-β-glucosidic bond and not to the presence of oxidized groups in the ring. The data listed in Table 5 and Table 6 have therefore to be regarded as real breaking of the polymeric chain, for TQ and Fe papers. For the samples treated with copper, they indicate the superposition of two effects: chain lowering and cleavage induced by measurement method, in the presence of oxidized groups in the pyranosic ring.

Figs. 13–15 plot the values:

$$\frac{1}{DP_v^{00}} - \frac{1}{DP_v^{t=0}} \quad \text{vs} \quad \frac{1}{DP_v^{t}} - \frac{1}{DP_v^{t=0}}$$

which represent respectively the number of scissions caused by oxidation and the total number of scissions (by hydrolysis and by oxidation). The relation between these quantities would be described as a 45° line if hydroly-

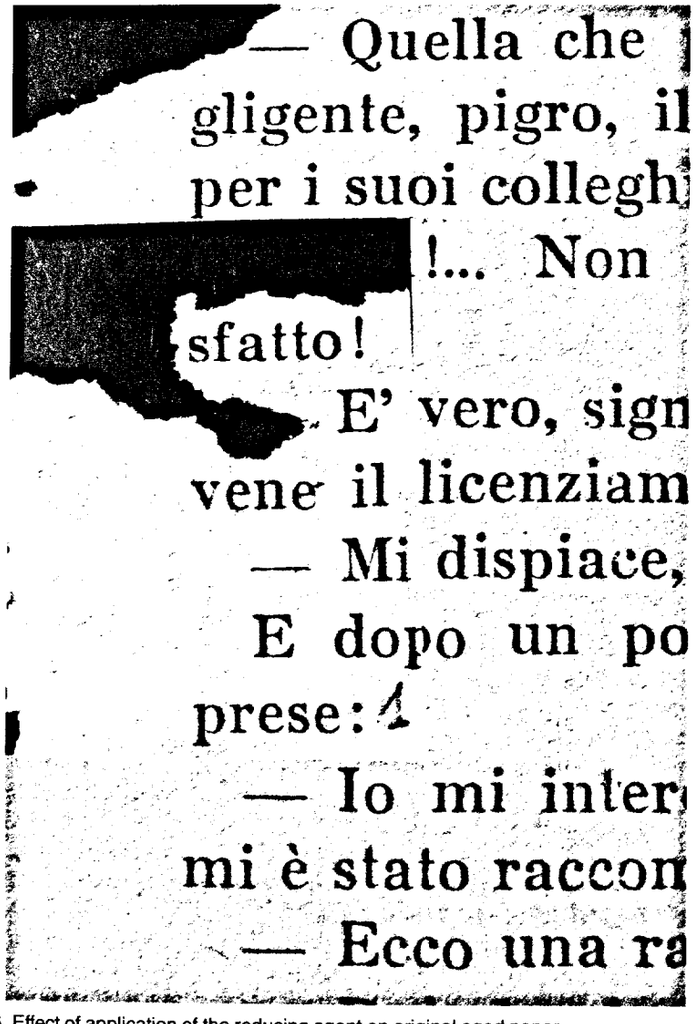

Fig. 16. Effect of application of the reducing agent on original aged paper

sis is the unique degradation mechanism. The higher the slope, the higher is the amount of oxidation.

We obtain slopes of: 38.5° for TQ papers, 41.9° for Fe papers and 81° for Cu papers. These values indicate that the iron-cellulose interaction leads

mainly to hydrolysis, whereas the copper treatment leads to an oxidation with cleavage of semiacetalic bond, followed by hydrolysis.

CONCLUSION

All experimental results point out that:

- Iron ions act as a catalyst for the cleavage of cellulose 1-4-β-glucosidic bond, whereas copper ions catalyst the oxidation on the anhydroglucose ring. The Lewis mechanism (Fig. 5), until now only postulated, is therefore experimentally verified.
- Measurements of average "cold" and "hot" degree of polymerization, statistically analyzed, coupled with the carboxyl content determinations, are good indicators of oxidative mechanisms in the cellulose degradation.
- The borane tert-butylamine complex has good reducing power and permits an optical bleaching of oxidized paper (Fig. 16).

The evidence of two different mechanisms for the iron-cellulose and copper-cellulose interactions induces us to discuss again deacidification: if the copper content in paper is high, the use of strong deacidification products can be dangerous for the paper conservation, inducing β-alkoxy elimination mechanisms. In this case it would be convenient to implement a preventive reduction.

We stress that it is necessary, before using the reducing agent, to test that dyes, especially those containing carbonyl groups, are stable with treatment.

ACKNOWLEDGEMENT

The authors would like to thank Professor Ludovico Santucci for the suggestion to use the method of "hot viscosity" measurements, which he conceived.

SUMMARIES

The Degradation of Cellulose with Ferric and Cupric Ions in a Low-acid Medium

Metallic cations play an important role in cellulose degradation. Different mechanisms have been proposed for cellulose-metal interaction: a free radical mechanism in which the metal acts as a catalyst in the homolytic scission of the cellulose peroxide and a Lewis mechanism that involves either the semiacetalic oxygen on the anhydroglucose unit or the β-glucosidic oxygen with formation of donor-accetor bonds. The first aim of our experimental work is to quantify the degradative effects induced by iron and copper ions in a low-acid medium and to verify whether experimental data are in agreement with one of the mechanisms proposed in the literature. All experimental results point out that iron ions act as a catalyst for the cleavage of cellulose 1-4-β-glucosidic bond, whereas copper ions catalyze the oxidation on the anhydroglucose ring and are in agreement with the Lewis mechanism, which has now been experimentally verified. The second goal is to determine whether the use of a reducing material can obstacle the oxidation catalyzed by metals, producing optical bleaching of paper. The borane tert-butylamine complex shows good reducing power and permits optical bleaching of oxidized paper.

La dégradation de la cellulose avec des ions de fer et de cuivre dans un milieu d'acides faibles

Les cations métalliques jouent un rôle important dans la dégradation de la cellulose, Différents mécanismes ont été proposés pour décrire l'interaction cellulose-métal: un mécanisme de radicaux libres dans lequel le métal agit comme catalyseur dans la scission homolytique des peroxydes de cellulose et un mécanisme de Lewis que implique l'oxygène semi-acétalique sur l'unité anhydroglucose ou l'oxygène β-glucosidique avec la formation de liaisons doneur-accepteur d'électrons. Le premier but de cette recherche expérimentale était de quantifier les dégradations de cellulose causées par des ions de fer et de cuivre dans un milieu d'acides faibles et de vérifier si les données expérimentales correspondent avec l'un ou l'autre des mécanismes proposés dans la littérature. Tous les résultats expérimentaux montrent que les ions de fer agissent comme catalyseur pour la scission de la liaison 1-4-β-glucosidique de la cellulose alors que les ions de cuivre agissent comme catalyseur de l'oxydation de l'anhydroglucose et sont en accord avec le mécanisme de Lewis qui a maintenant été vérifié expérimentalement. Le deuxième but était de déterminer si l'utilisation d'agents réducteurs peut empêcher l'oxydation catalysée par des métaux tout en réalisant le blanchiment du papier. Un complexe du bore, le t-butylamineborane, (formule: $(CH_3)_3CNH_2 \cdot BH_3$) montre un bon pouvoir réducteur et permet le blanchiment du papier oxydé.

Der Abbau von Cellulose unter dem Einfluß von Eisen- und Kupferionen im schwach sauren Medium

Schwermetallionen sind von großer Bedeutung beim Abbau von Cellulose. In der Literatur werden verschiedene Mechanismen hierfür vorgeschlagen: einmal ein Vorgang an freien Radikalen, wobei das Metallion als Katalysator für die homolytische Spaltung über Peroxi-cellulose wirkt, zum anderen ein Mechanismus nach Lewis, der entweder den Sauerstoff des Halbacetals an der Anhydroglucoseeinheit oder den des β-Glucosids unter Bildung von Donor-Acceptor-Bindungen einbezieht. Eines der Ziele der Untersuchung was es, den von Kupfer- und Eisenionen im schwach sauren Medium ausgehenden Abbaueffekt quantitativ zu erfassen und festzustellen, ob die experimentellen Feststellungen im Einklang mit den in der Literatur unterstellten Vorgängen stehen. Alles weist darauf hin, daß Eisen als Katalysator für die Kettenspaltung an der 1-4-β-glucosidischen Bindungsstelle und Kupfer für die Oxidation im Anhydroglucoserings wirkt, was dem Mechanismus nach Lewis entspricht, der damit experimentell erwiesen ist. Sodann wurde untersucht, ob eine Behandlung mit Reduktionsmittel die von Schwermetall katalysierte Oxidation hemmen kann, was auch einen Bleichwirkung auf das Papier hätte. Der Boran-tert-Butylamin-Komplex zeigte gute Ergebnisse; er bewirkt ein optisch wahrnehmbares Aufhellen von oxidiertem Papier (Formel $((CH_3)_3CNH_2 \cdot BH_3)$.

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Results of the Paper Splitting Process

by J. LIERS, W. WÄCHTER & G. MÜLLER

Introduction

Paper splitting is an excellent method of restoring paper where damage to the whole object is extreme.[1–3] Damage can have been caused by mechanical, chemical or biological factors. By using this method, it is possible to stabilise the sheet of paper mechanically and to conserve the paper by inserting an alkaline buffer and a fungicide if necessary. This would prevent future deterioration in the paper from acids, ink corrosion or mildew. The empirical experiences of restorers who have used this method confirm these observations.[1,2,4] But how far can the strength of paper be increased? And how can this method be compare with other restoration methods from the point of view of mechanical stabilisation and chemical conservation?

This article quantifies the results of paper splitting in comparison with other paper restoration and conservation methods.

Experimental

Test materials used

We investigated three different test papers (Table 1). Paper-1 was a 20-year-old acid-sized paper with minor damage. Paper-2 was a similarly composed material but had an ageing time of 120 years. For a modern library, these two materials represent the typical problem of damage caused by the acid decomposition of paper.

Paper-3 showed damage typical of old manuscripts with handwriting. Although the old paper was permanent because it was made of rags and produced by gelatine sizing, it was badly damaged by ink corrosion.

Conservation methods used

Table 1 gives an overview of the conservation methods used. The tools used for the treatments described in this article were explained in a previous article.[3] The treatment of Paper-1 was undertaken at the German Library in

Table 1. The test material and the conservation method used

paper	origin	description	damages	methods of treatment
1	journal "Deutscher Drucker" printed: 1972	paper made of wood pulp; weight=69 g/m2	paper yellowed; margin is brittle	– wet treatment – splitting – resizing*
2	newspaper "Nationalzeitung"; printed: 1875	paper made of wood pulp; weight=52 g/m2	damages by acid deterioration; paper is very brittle	(– wet treatment) – splitting – lamination*
3	manuscript with handwriting; written: 17th c.	paper made of rags	damages by ink corrosion; part with writing is very brittle	– splitting – wet treatment

*Treatment alternative to the splitting process

Leipzig and the treatment of Papers-2 and -3 at the Thuringian University and State Library.

Paper-1

The first conservation step was the wet treatment. The paper was washed in desalinated water at 70-80°C for 30 minutes. It was then treated in a reducing bath with an aqueous solution of 0.02 wt.-% sodium hydridoborate at a temperature of 30°C. After raising the temperature to 55°C the leaves were removed from the bath. The leaves were then rinsed and dried.

After drying, some samples of the paper were resized and others were split.

The process of splitting was described in detail in the article on the process of paper splitting.[3] We used the paper splitting machine to prepare these samples.

For the process of resizing we used an aqueous solution of 1.5% methyl cellulose, 1.5% carboxy methyl cellulose, 0.2% calcium carbonate and 0.2% magnesium carbonate. After this process, the acids in the paper were neutralised in a saturated aqueous solution of calcium and magnesium hydrogencarbonate. Finally the sheets were dried and pressed.

Paper-2

This paper was treated in two ways: some of the leaves were split and the others were laminated.

Before splitting, the paper was washed in hot water as described for Paper-1. The partially mechanised method was used for the process of splitting.[3]

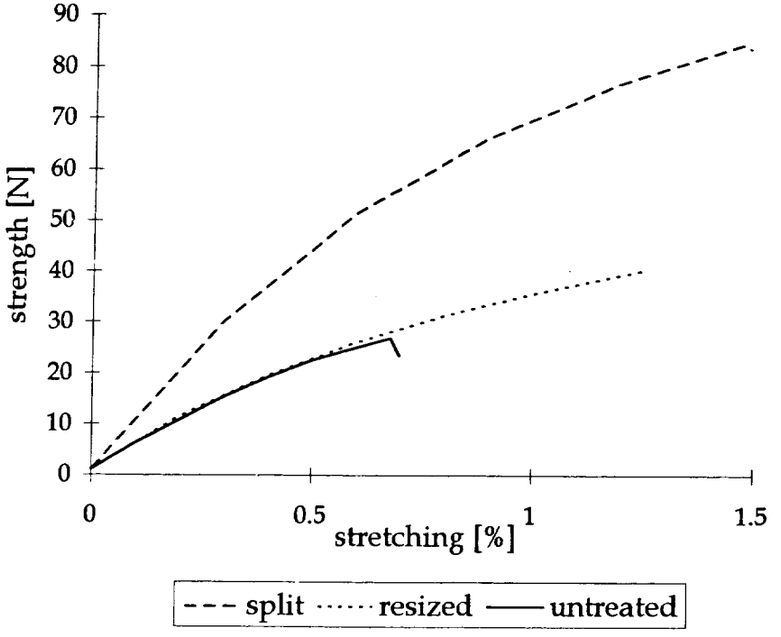

Fig. 1. Strength according to the stretching of differently treated samples of Paper-1.

Before lamination, the paper was not pretreated. We used Filmoplast R (Neschen company) for the lamination process. Filmoplast R is a tracing paper coated with a hot setting adhesive. Magnesium carbonate was added as alkaline buffer to this adhesive.

Paper-3

Because of the danger that the inks might run in water, the first treatment step was the paper splitting process. The partially mechanised method was used.[3]

After splitting, the ink was fixed by the glue of the core material which was partly diffused to the surface of the paper in the couching step. Washing in hot water was therefore possible as the final treatment.

Test methods used

From samples of untreated and treated materials, we determined the tensile strength (in machine (Papers-1, -2) or rib direction (Paper-3)), the pH-value

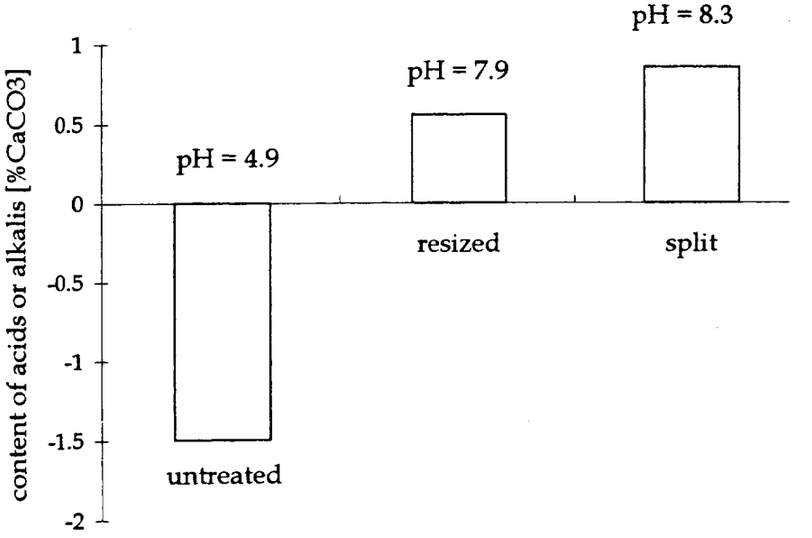

Fig. 2. The pH-value and the acid or alkali content in untreated and treated Paper-1.

and the acid or alkali content. The tensile strength was determined according to DIN 63112[5] and the pH-value according to DIN 53124.[6] For the determination of the acid or alkali content, basic titration was used. The values were converted into a deficit or surplus of $CaCO_3$ to illustrate the content.

Results

Paper-1

Fig. 1 shows the paper strength. This was measured by stretching different samples of Paper-1: untreated, resized and split paper. Resizing improved the stability of the paper slightly, but splitting dramatically increased the tensile strength. There is a remarkable difference in the strength curves. The curve of the resized paper followed the first part of the curve of the untreated paper whereas the curve of the split paper reached a completely different range of strength and elasticity.

Fig. 2 shows the pH-value and content of acids or alkalines in the untreated and treated paper. Both methods of treatment, the resizing (in comparison with the wet treatment) and the paper splitting, were able to deacidify the paper. During the process of paper splitting a higher content of alkaline was inserted into the paper.

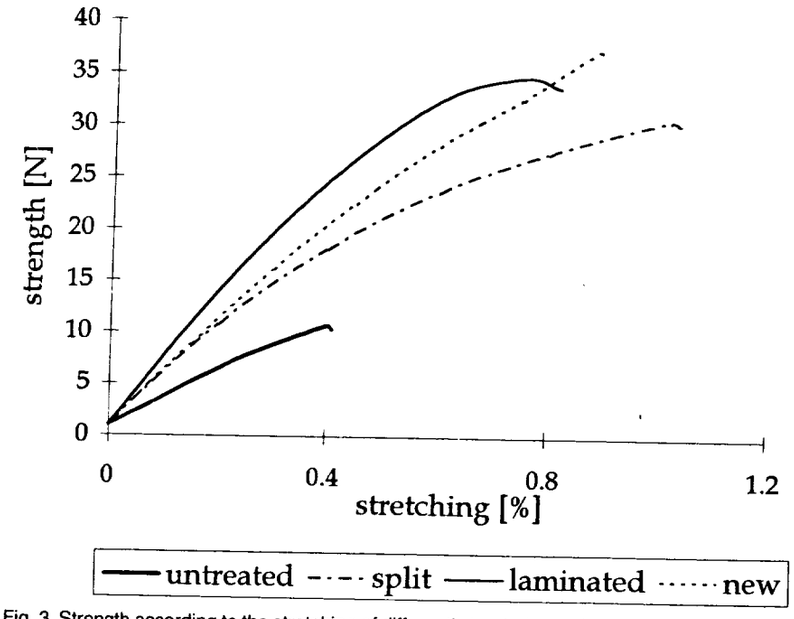

Fig. 3. Strength according to the stretching of differently treated samples of Paper-2 and of new paper.

Paper-2

Strength was determined according to the stretching of samples of Paper-2: untreated, laminated and split paper (Fig. 3). For comparison, a new newspaper was tested as well. As the diagram shows, lamination and splitting dramatically increased the tensile strength and the elasticity of the paper which reached values similar to those achieved by the new paper.

Fig. 4 shows the pH-value and the content of alkaline buffer in untreated, split and laminated paper. The split paper had a pH-value of over 7 and contained an alkaline buffer whereas the pH-value of the laminated paper was below 7.

Paper-3

Fig. 5 illustrates the strength (measured by stretching) of samples of Paper-3: untreated and split paper. For comparison, new paper made of rags was tested as well.

As this figure shows, the inner part of the untreated paper was badly damaged by ink corrosion whereas the unwritten part of the paper was in better

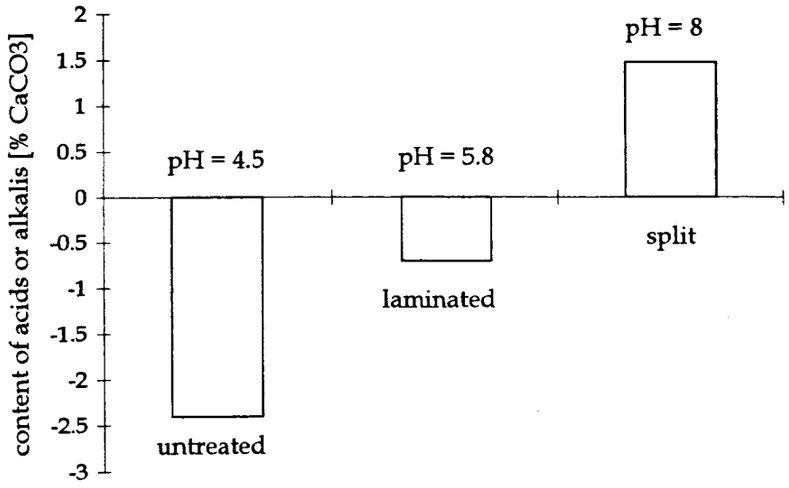

Fig. 4. The pH-value and the acid or alkaline content in untreated and treated Paper-2.

condition. The process of paper splitting improved the tensile strength and the elasticity of all parts of the paper. The less damaged margin of Paper-3 reached values after splitting that were comparable to the new paper, tested for comparison.

The pH-value and the content of alkaline buffer of the untreated, split paper are shown in Fig. 6. The written inner part of the paper was severely acidic because of the ferro-gallus ink used, whereas the margin of the paper was only slightly acidic. After the processes of wet treatment and paper splitting the whole paper was alkaline and contained a buffer of $CaCO_3$.

Discussion

As the tests with the differently treated samples of Paper-1 have shown, paper splitting and resizing combined with the wet treatment are able to both strengthen and deacidify. However, the process of paper splitting made it possible to raise the strength of the paper to much higher levels. Also a slightly higher alkaline content was introduced into the paper from an adhesive and core paper that contained alkaline.

For strengthening slightly damaged paper (like Paper-1), the process of paper splitting is a possible but not necessary method. The wet treatment in connection with resizing is both sufficient and more efficient.

For strengthening very brittle paper (like Paper-2) which may have addi-

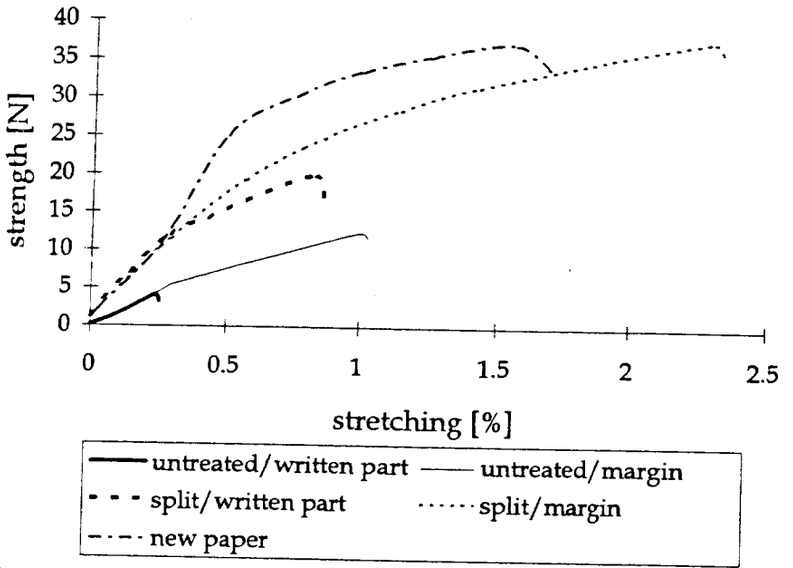

Fig. 5. Strength according to the stretching of treated and untreated samples of Paper-3 and new paper made of rags.

tional tears in some parts, paper splitting is the more effective of the two methods.

Another method capable of stabilising such damaged paper is lamination. However, as Fig. 4 shows, treatment by paper splitting not only stabilises the paper from a mechanical point of view, it also deacidifies the paper which gives it a high ageing resistance.

In addition, the paper splitting process (unlike lamination) preserves the texture of the original, leaving the surface of the paper and its readability unchanged. Even watermarks are preserved. Another advantage of paper splitting as opposed to lamination is its reversibility.

The treatment of Paper-3 shows the possibilities of paper splitting in the restoration of paper with very specific damage. Additional deacidification from the treatment makes the paper resistant to further corrosion by the ferro-gallus ink.

The restoration of paper with very specific damage (caused by mildew, insects, or dye and ink corrosion) is possible with paper splitting because of the flexibility of the process.

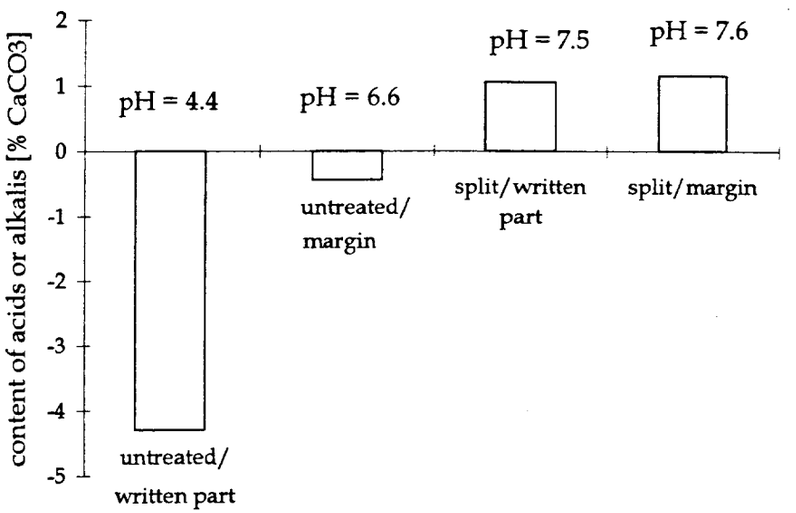

Fig. 6. The pH-value and the acid and alkaline content in untreated and treated Paper-3.

Conclusion

These three examples show part of the application of paper splitting. They demonstrate that this process is an excellent method of stabilising paper with very different kinds of damage. The restored materials are additionally conserved by the insertion of an alkaline buffer into the paper through the core material and adhesives used.

By varying the core materials and the composition of the adhesive, paper splitting can be tailored to the specific damage of the object. The influence of the materials used in paper splitting on the results should be further investigated.

In addition to this, paper splitting is reversible and preserves the texture of the original.

Mechanisation of the splitting process will reduce both the cost of and the risks in this method. The cost of splitting one page will further decrease with the paper splitting machine. We are therefore hopeful that the process of paper splitting will play an important role in paper restoration in the future.

Summaries

Results of the paper splitting process

This article quantifies the results of paper splitting. Three different test papers were treated with different restoration methods such as paper splitting, resizing and lamination. After treat-

Results of the Paper Splitting Process

ment the pH-value, the alkali content and the tensile strength were determined. This article demonstrates that paper splitting is an excellent method of stabilising paper with very different kinds of damage. The restored materials are further conserved with the insertion of an alkaline buffer into the paper.

Résultats du procédé "paper splitting" (fendage du papier)

Cet article quantifie les résultats du paper splitting. Trois différents papiers test ont été soumis à des traitements de restauration distincts: paper splitting, réencollage et lamination. Après traitement, on a mesuré le pH, la quantité d'alcalis et la résistance à la traction. Cet article montre que le paper splitting est un excellent moyen pour stabiliser un papier présentant différents types de dommages. En outre, une réserve alcaline est insérée à l'intérieur du papier des documents restaurés.

Ergebnisse des Papierspaltens

Der Aufsatz quantifiziert die Ergebnisse des Papierspaltens. Drei verschiedene Versuchspapiers wurden nach verschiedenen Methoden behandelt: Papierspalten, Nachleimen und Laminieren. Nach der Behandlung wurden pH, Alkaligehalt und Zugfestigkeit gemessen. Es wird gezeigt, daß das Papierspalten eine hervorragende Methode zur Festigung von Papier mit sehr verschiedenartiger Schädigung ist. Die behandelten Objekte werden dabei auch durch den Einbau eines alkalischen Puffers konserviert.

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A Pollution Chamber for the Accelerated Deterioration of Materials

by FLOREAL DANIEL

Introduction

Extensive research carried out since the 1930s has demonstrated the degrading effect of atmospheric pollution on paper and the importance of accounting for this factor in the evaluation of documents conserved in libraries and archives. Over the last 10 years, the French Centre for Research into the Conservation of Graphic Documents (CRCDG) has led research into the effect of SO_2 and NO_2 pollution under varying conditions of concentration, temperature and humidity.[1,2]

One of the first investigations into the effect of pollutants on paper was carried out by Kimberley,[3] who demonstrated that the exposure of paper at concentrations between 2 and 9 ppm over 10 days made the paper fragile and diminished its folding resistance. Shortly after, Jarell and coworkers[4] exposed papers to town gas containing 8 ppm SO_2 and found evidence of variations in the alpha-cellulose levels, the copper number and the resistance to folding and acidity.

During the 1960s, Hudson & Milner[5] used labeled sulfur at concentrations of the order of 0.5-1.0% with the aim of evaluating its absorption on paper. Edwards[6] tried to link natural aging conditions with artificial exposure conditions.

Up until the 1990s, researchers focused on the use of SO_2 alone. Some studies in the last 10 years have, however, examined the effect of SO_2 and NO_2 combinations on papers.

Previous research on pollution in the 1980s at CRCDG were performed with simple equipment using permeation tubes of SO_2 and NO_2.[7] From this first equipment a pollution apparatus was derived in 1991 the which has permitted the CRCDG to participate in three European research programs on the effects of pollution of the paper and leather.[8-10]

This equipment has three independent exposure chambers for the pollution of materials under the following conditions:

- SO_2 and NO_2 concentrations at the entrance to the chamber of 0 to 50 ppm

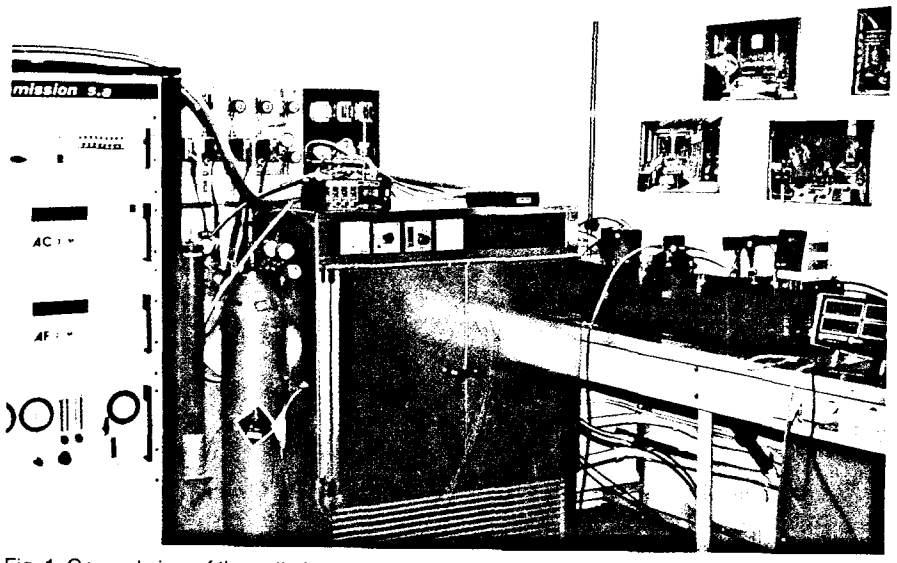

Fig. 1. General view of the pollution equipment at CRCDG.

- temperature: 0 to 60°C±0.5°C
- relative humidity: 40 to 90%±2%
- total flow rate: 220 l/hour
- continuous use possible for a period of 1 to 6 weeks.

The room in which the apparatus is installed is thermally regulated at 20°C. The relative humidity does not need to be controlled because there is no interaction between the ambient air and the pollutant circuit.

Pollution Chamber

The pollution chamber is made of Plexiglas and has a capacity of about 130 liters. It can hold 100 sheets of paper of A4 format spaced at 4 mm. The homogeneity of the circulation and concentration of gases is obtained by a sliding plate perforated with 3-mm-diameter holes. This plate acts as a diffuser.

The gases must cross the chamber in such a way that there is a uniform flow throughout the volume in use. Usually, the gases cross the diffuser at a low flow rate (220 l/hour), which gives a circulation rate of 15 mm/min inside the chamber. This is slow enough to yield a laminar flow between the sheets. The rate of air renewal in the chamber can be 0.5 to 2.

The samples are kept in place with 200 Plexiglas rods (20 cm long, 3 mm diameter) which are fixed in holes 4 mm apart and aligned in four rows.

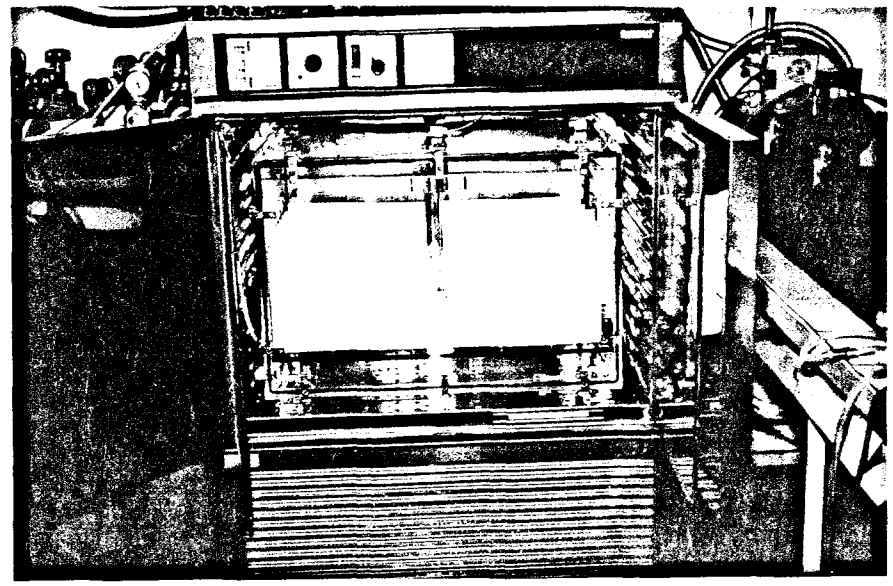

Fig. 2. Exposure chamber.

Plexiglas was chosen for the interior accessories since it is easy to manipulate and is relatively stable in the presence of the pollutants.

The gases are sampled and accounted for.

Gas Analysis

Gas samples for analysis are taken from the interior of the chamber and at its entrance and exit, in order to verify the homogeneity in the concentration of SO_2 and NO_2. It is also possible to determine the quantity of pollutants absorbed by the paper since we know the flow rates of the gases and can measure their concentrations at the entrance and exit.

The transfer lines between the apparatus and analysis unit are constructed so as to reduce the risk of condensation and absorption, which would give false measurements. It is thus necessary to heat the tubing so that its temperature is always above dew-point.

The passage of the sample gas in the chamber is controlled by electronic valves operated by a series of interlocking buttons. This set-up is integrated into the analysis unit.

The analytical measurements are carried out using fluorescence UV for SO_2 and chemiluminescence for NO/NO_x (respectively AF 21 M and AC 31

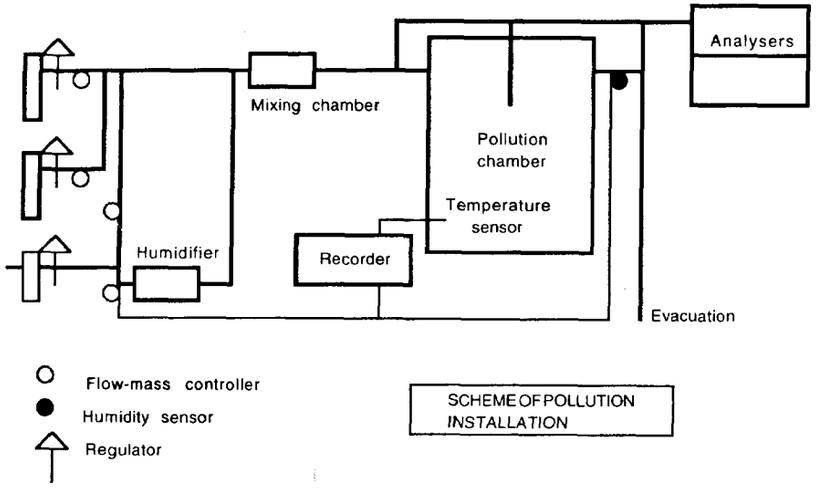

Fig. 3. Pollution equipment at CRCDG.

M by Environment SA). The analyzers are able to measure a range of concentrations of 0 to 10 ppm. As we use concentrations higher than this, the gases must be diluted before being introduced into the analyzers. The dilution ratio used is 1:60.

The minimum detectable concentration for this equipment is of the order of ppb. However, with the injection mode used in the dilution system, the actual sensitivity falls to 0.1 ppm. The instruments are calibrated with dry air for the zero-point and with cylinders of standard gas mixtures of $NO_2/N_2/O_2$ and $SO_2/N_2/O_2$ with a concentration of 50 ppm±0.1 ppm.

Pollutants

The concentration of pollutants is regulated in the test chamber by mixing air with high-concentration pollutants.

Before introduction to the chamber, the air is dried and purified using a high-efficiency Ultrapac drier MSD 004.

The pollutants introduced into the pollution chamber are supplied by cylinders of SO_2 and NO_2 at 1% concentration in an N_2/O_2 (80:20) mixture.

For a concentration in the chamber of 50 ppm and a total flow rate of 6 l/min, the flow rate of NO_2 or SO_2 must be 30 ml/min. The lifetime of the cylinder is thus six weeks for NO_2 and four months for SO_2.

The cylinders are placed in a ventilated cupboard connected to an extractor operating at 80 m^3/hour. A purge system is used to empty the line

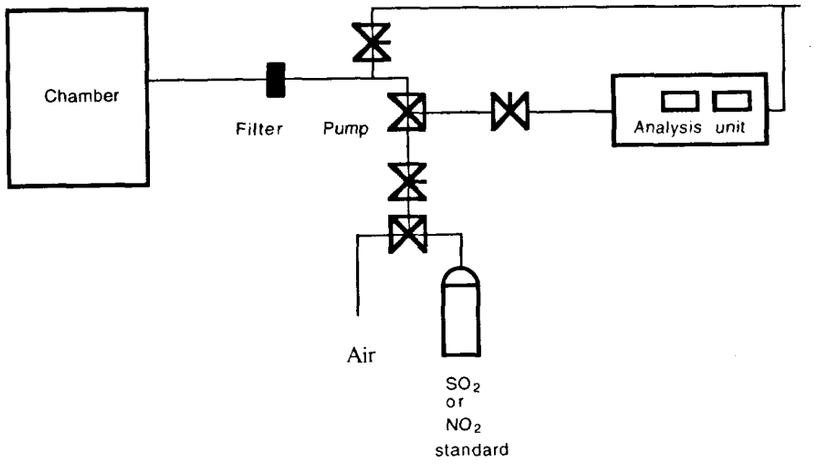

Fig. 4. Gas analysis circuit.

of the air it contains and to maintain the purity of the gas. This also guarantees the safety of the operator during cylinder changes. The pollutant gases travel to the flowmeters through rigid stainless-steel tubes. After the flowmeters, Teflon tubing is used. The tubes between the chamber and the analyzer are heated to prevent condensation, which would disturb the analysis. The evacuation of gases at the exit of the chamber occurs via larger diameter tubing, which is linked to a fume hood.

We use flow-mass controllers with display units and their own power supply with four channels. This allows good precision and facilitates the control and calibration of the flow of a pollutant as a function of its concentration in the chamber. The minimum controllable flow is 0.3 ml/min for the pollutants and 30 ml/min for air (dry or humid). The four flowmeters necessary for each chamber are mounted on a deck placed in close proximity to the chamber concerned in order to ease the control of the flow and reduce the response time.

The display and control of flow are carried out using the display unit. Each chamber has its own control system mounted on a rack with the systems used to measure the temperature and the relative humidity in the chamber. The display and control units can be used to fix the flow of SO_2, NO_2, and dry and humidified air. The flowmeter can be controlled manually as a function of the relative humidity.

Even though the mixing in the line, i.e., simply in the valves and tubes along the route taken by the gases, probably gives a sufficiently homogene-

ous mixture, the gases (pollutants, dry air, humid air) are thus passed through a three-necked flask filled with coils (a sort of chicane) immediately before their entrance to the chamber.

When the adjustment of the flows permits a concentration of 30 ppm in the inlet of the chamber, the variations of concentration during 24 hours are lower than 1% for SO_2 and 3% for NO_2.

The inertia of the chamber represents the time necessary to have the same concentration in the outlet as in the inlet. It depends on the total flow and thus on the ventilation rate of the chamber. The flow maximum usable in the chamber is 4 l/min. With this condition, the inertia of the chamber is lower than 2 hours.

Humidification and Control of the Temperature

The chamber is situated in a thermostated oven (Memmert model BKE40) in which the temperature can be varied between 0 and 60°C with a precision of ±0.5°C.

The independent humidification system is based on the exchange of water vapor between the air flow and the surface of water in a closed chamber. Because of the low rates of air flow used, this system can yield air with a humidity of 100%. This air, which is saturated with vapor, is then mixed with dry air contaminated with pollutants. The desired relative humidity is thus obtained by varying the flow of humid air relative to that of dry air using two electronic flowmeters operating at 0 to 3 l/min.

It is not advisable to use humidity detectors with sensitive elements based on polymer films since these deteriorate in the presence of the pollutants used. The humidity is therefore measured using a cold platinum mirror sensor (General Eastern Hygro M2).

Platinum sensors of the type PT 100 are recommended for the measurement of the temperature in the interior of the chambers.

The graph below shows the variations of relative humidity in the chamber as a function of time and for the following flows: dry air 0.5 l/min, humid air 0 to 0.7 l/min.

The minimum relative humidity (no humid air added) in the chamber is 15% because there is contact in the mixing flask between the dry air flow and the stagnant humid air in the humidification system.

When we start with dry air in the chamber (the worst condition), we need 8 hours to reach a relative humidity of 50%±2%.

We have a calibration of the relative humidity reached versus the humid air flows for a constant flow of dry air (0.5 l/min) (Fig. 5).

When the flows are adjusted to get 50% relative humidity, the amplitude of the RH variations is about ±2%.

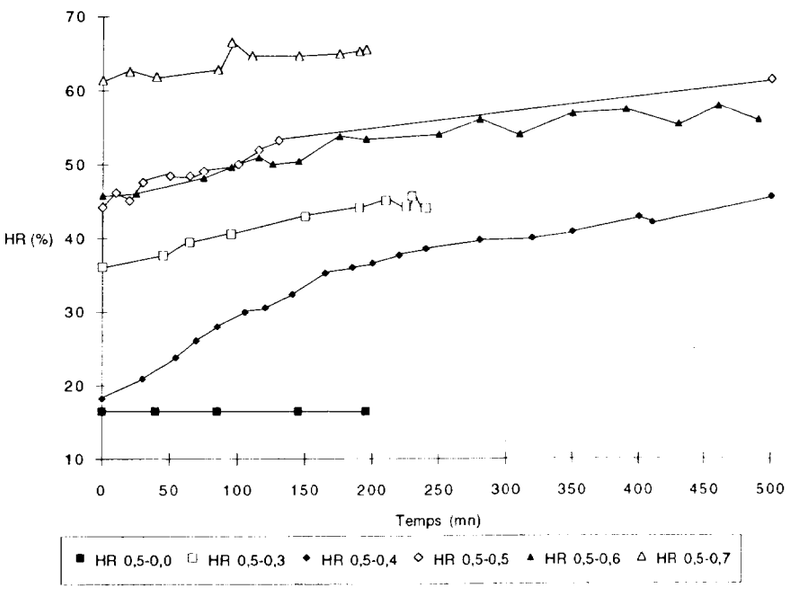

Fig. 5. Relative humidity in the exposure chamber as function of the flow of the gases and time.

In order to control the influence of moisture on the concentration of pollutants in the inlet of the chamber, we fixed the dry and humid air flows to reach 50% relative humidity in the chamber, and for different flows of SO_2 we followed the SO_2 concentration and its influence on the relative humidity in the chamber. The ratio of the SO_2 flow and the concentration is the same in the presence of dry and of moist air. The relative humidity is not affected by the presence of pollutants.

With a concentration of pollutants of 30 ppm (SO_2 and NO_2) and the minimal relative humidity, we need 6 minutes to get a stable measurement of the concentration of the pollutants. This time represents the inertia of the analysis system (analyzers and gas circuit).

There is no effect from the flow of one of the pollutants on the concentration of the other pollutant.

Data Storage

The data collected during the exposure of the samples in the chamber (relative humidity, temperature, pollutant concentrations) are stored using an Apple Macintosh IIsi computer equipped with an analog MAC ADIOS II Jr card

(16 channels) and the data-acquisition program Labtech Notebook. The data are recorded continuously and can be used later for statistical treatment.

Exposure of the Samples

The samples are prepared beforehand in a climatized chamber at 23°C and at 50% RH for at least 48 hours. They are then placed in the chamber overnight with the desired temperature and humidity levels, but in the absence of pollutants. The pollutants are introduced the next day. After exposure, these operations are carried out in reverse.

The chamber is pre-conditioned with a mixture of dry and humid air in order to adjust the flow, temperature and relative humidity to the required levels. The gases are then introduced into the chamber. This pre-conditioning step means that the desired pollutant concentrations are obtained immediately upon entry into the chamber. The time taken to charge the chamber is thus taken as the time necessary to obtain the same concentration at the exit and the entrance of the chamber in the absence of samples. Because of the low flow rates of the gases, this time is about 1 hour.

The pollutant concentration in the gas is displayed at the beginning of the exposure of the samples at the entrance of the chamber. It is possible to vary the flow of the pollutants while keeping their concentrations the same. In this case the degradation of the exposed material will be modified. This effect will be studied in the future.

Conclusion

The experience of running the apparatus continuously over 3 years has permitted a worst-case assumption of 10% of the total running time lost due to breakdown or maintenance. During the entire life of the apparatus, the only breakdown was due to the failure of a cylinder of NO_2 that was used to feed the chamber. The risk of such a breakdown is now significantly reduced as we have installed a second ventilated cupboard stocked with gas cylinders which can automatically replace a failed cylinder.

With this equipment we have performed research on the degradation of different materials (paper, leather, parchment, photographs), on conservation products (storage boxes) and restoration methods.

This equipment is in constant evolution. We are currently adapting a system for the production and control of polluted environments with concentration levels of hundreds of ppb, for further research on the effect of pollution concentration on the deterioration of materials.

Also, because few data are available on the effect of ozone on the conservation of graphic documents, we will complete our equipment with an ozone generator and analyzer.

Summaries

A pollution chamber for the accelerated deterioration of materials

The article describes the construction and function of an apparatus which ensures a regular flow of air with a given concentration of gases constituting air pollution (SO_2, NO_2) and of humidity at constant temperatures over a period of up to six weeks. The data are recorded by computer and can be used for statistical analysis. In the central chamber (130 liters) about 100 sheets of A4 paper can be treated so as to imitate and accelerate their exposure to highly polluted air.

Une chambre de pollution pour la dégradation accélérée de matériaux

On décrit la construction et le fonctionnement d'un appareil dans lequel on peut établir un flux d'air régulier avec une concentration donnée de gaz polluants (SO_2, NO_2) et d'humidité à des températures constantes pendant une période allant jusqu'à six semaines. Les données sont enregistrées par ordinateur et peuvent être traitées statistiquement. Dans la chambre centrale (130 litres) environ 100 feuilles de papier format A4 peuvent être traitées de façon à imiter et à accélérer leur exposition à une atmosphère fortement polluée.

Eine Begasungskammer zur Beschleunigung der schädlichen Wirkung von Umweltverschmutzung auf Materialien

Es wird die Konstruktion und die Wirkungsweise einer Anlage beschrieben, in der über Zeiträume bis zu sechs Wochen ein gleichmäßiger Strom von Luft eingestellt werden kann, die Umweltgase (SO_2, NO_2) und Feuchtigkeit in konstanter Konzentration enthält. Die Meßwerte werden über Computer erfaßt und können statistisch ausgewertet werden. In der Behandlungskammer (130 l) können ca. 100 Blatt Papier A4 einer Imitation und Beschleunigung der von der Umweltverschmutzung ausgehenden Schäden ausgesetzt werden.

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2. Hon, D. N.-S.: *Yellowing of modern papers*. In: Williams, J. C., ed. *Preservation of paper and textiles of historic and artistic value II*. Advances in Chemistry Series, 193. Washington, DC: American Chemical Society, 1981: 119–42.

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