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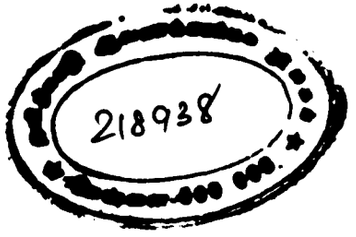

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Fourier Transform Infrared Spectroscopy Applied to the Analysis of Ancient Manuscripts

by M. CARME SISTACH, NÚRIA FERRER & M.T. ROMERO

INTRODUCTION

Infrared spectroscopy is applied to the characterization of compounds. The technique is based on the interaction of infrared radiation with matter. The result is a spectrum with absorption bands corresponding to the different vibrations of the molecules. Each molecule has a specific spectrum in the infrared range, i. e. a fingerprint. Therefore, the technique has been used extensively for the identification of molecules in all kinds of samples: liquids, solids and gases. Conventional equipment using dispersive infrared radiation had some disadvantages due to the loss of energy caused by their optical design. Moreover, time is also an important factor, because points in spectra are obtained in succession along the wavenumber. Nowadays Fourier transform infrared spectroscopy has replaced the old systems, allowing a better throughput of energy, faster scanning and therefore an improvement in the signal-to-noise ratio. These advantages allow the use of different accessories coupled to the infrared instruments such as diffuse and attenuated total reflectance, microscope, photoacoustics, etc.

Although infrared spectroscopy has been widely used in chemical industries, chemical synthesis research, forensic analysis and other research fields, its application to conservation problems is growing, especially after the coupling of microscopes to the spectrometers[1–3]. This allows a variety of applications including analysis of pigments, varnishes, textiles, papers, inks, corrosion products, etc.[4–7] in very tiny samples and in all kinds of matrices. Analysis of paper using infrared spectroscopy has been described elsewhere[8–11].

In our laboratory different samples related to problems of conservation have been analysed in the last decade: oxidised papers, ancient pigments in pictures, synthetic and natural fibres, ancient wall papers from old buildings, impurities in diamonds, amber, oils in paintings, archeological samples, inks, etc. Most of the samples analysed are unique and valuable, and it is often impossible to remove even a very small amount from the matrix. This means that the infrared microscope is one of the alternatives most frequently used in our laboratory. Two

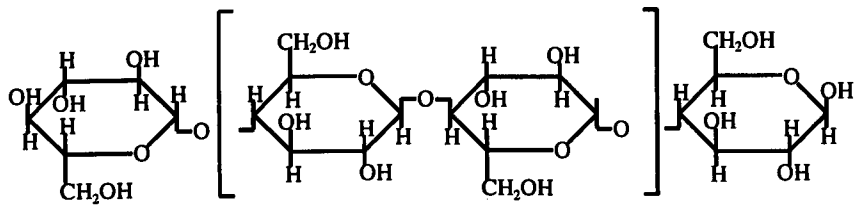

Fig. 2a: Molecule of cellulose.

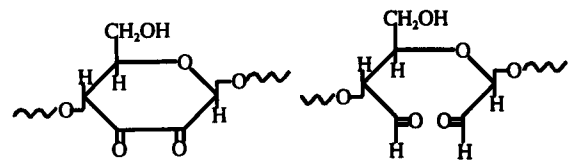

Fig. 2b: Oxidized groups in C_2 and C_3.

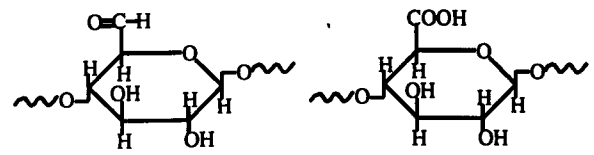

Fig. 2c: Oxidized groups in C_6.

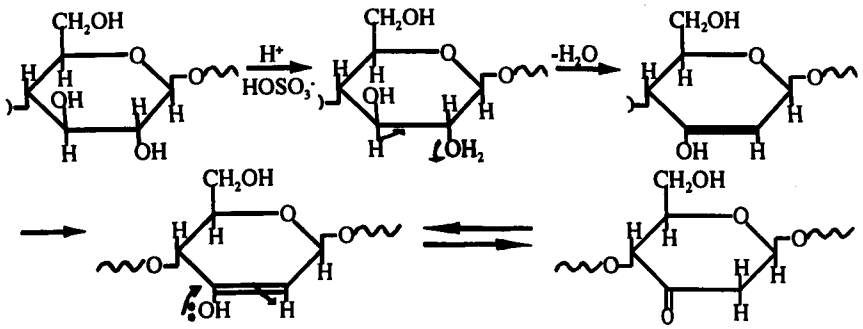

Fig. 3a: Acidic dehydration in C_2 and C_3 by E1 mechanism.

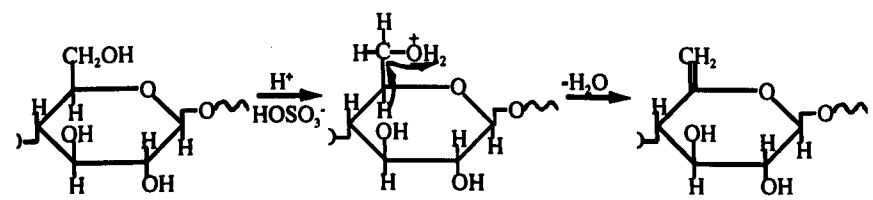

Fig. 3b: Acidic dehydration in C_6 by E1 mechanism.

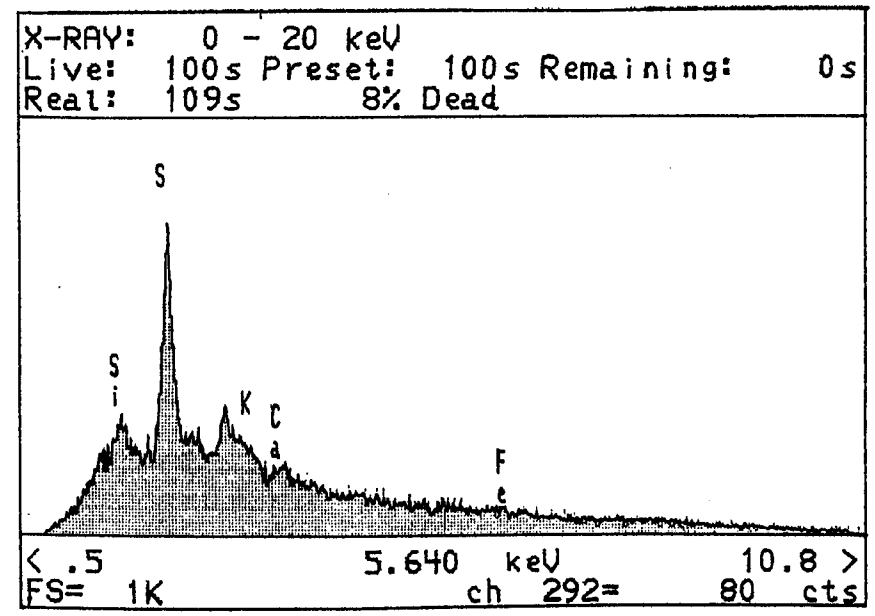

Fig. 4: SEM-EDX spectrum of the sulphur kept into one fibre.

as alum (Al-K-sulphate) which was used at the end of the XVIIIth century and rosin (abietic acid). Both components were added because paper was becoming thinner and alum also participates helping to deposit the gelatine glue and making the paper stronger.

DEGRADATION OF CELLULOSE

Two processes act against cellulose: oxidation (Fig. 2) and hydrolysis. Both, together participate in cellulose degradation. Alcohols can be dehydrated by sulphuric acid with mechanism E_1. The secondary C–OH and the primary C_6–OH in the piranose units of glucose can participate in dehydration. This reaction gives the alkene compound in C_6 and the ketonic group in C_2 or C_3, (Fig. 2 and 3). Both compounds are more reactive than non-dehydrated cellulose. Probably sulphur found in the fibres by SEM-EDX corresponds to the penetrating sulphuric acid (Fig. 4).

main analytical methods are used with the microscope. The first consists of removing a very small amount of sample from the matrix, normally a 20 micrometers particle is enough, and pressing it between two diamond windows, so as to spread the sample and produce a thin film that can be measured by transmission. The second method is used when it is not possible to remove particles from the matrix, and it is necessary to use the attenuated total reflectance objective, which is pressed against the surface of the sample. These methods, together with the conventional ones, allow the analysis of the most of the samples that we receive in our centre.

PAPER COMPOSITION

Paper is the most useful material kept in historical archives. Characteristics of paper depend on the origin of the fibre used to produce the paper, the alkaline buffering, the gluing, the rosin and the lignin. This last component was added when wood cellulose was used since the middle of the XIXth century.

Cellulose is the chemical compound involved in the fibre composition. This polymer is formed by units of glucose bonded with 1–4ß bonds. Polymerization gives a linear molecule with cyclic glucose units, which have three hydroxyl groups in carbons C_2, C_3 and C_6.

The oxidative degradation of cellulose interferes with the hydroxyl participation in the formation of H-bondings by cellulose chains. The –OH groups of the C_3 carbons are the less reactive because all of them participate in H-bonds. Although C_6–OH should be the most reactive, the hydroxyls in C_6 and C_2 have similar reactivities. This reduction of reactivity in –OH placed in C_6 is caused by its contribution to H-bondings. The oxidation of C–OH groups causes the partial destruction of H-bonds, as a consequence, the stability of cellulose decreases. In addition, the hygroscopic capacity of cellulose fibres is related to the number of hydroxyl groups: if the cellulose is more oxidized, its hydration capacity decreases.

Two processes are involved in cellulose degradation: acidity and oxidation. Paper acidity and oxidation in archived documents can be caused by iron gall inks and also by other factors such as abietic acid and added alum during paper manufacture. Catalytic oxidation by radical mechanism is broken out by metallic ions such as iron and copper that bring about cellulose oxidation[12]. This oxidation affects the hydroxyl groups, therefore the stability of the cellulose molecule changes and also changes its crystallinity.

Acidity causes cellulose hydrolysis. Iron gall ink keeps sulphuric acid which is a by-product of the ink. This acid can go through the paper and penetrates into

Fig. 1: Degraded fibres from an acidic manuscript.

the fibres when this ink is used in writing[13]. The hydrolysis of the cellulose caused by acidity and oxidation breaks out its depolymerization and this affects the fibres stability whose easy breakage could be tested by optical microscopic images (Fig.1).

Craftsmen who made ancient papers used only rag fibres from linen, hemp and sometimes cotton until the middle of the XIXth century. The use of wood cellulose starts in 1850 and lignin impurities appear in the paper because its phenolic compounds are degraded by light and cause ageing phenomena of darkening in the paper. Fillers in ancient archived manuscripts are mostly calcium carbonate.

Arabian craftsmen glued the paper with starch from rice or wheat[14–16]. Since 1350 the Italian paper starts to come to Catalonia, and this Italian paper was manufactured in a different way compared to the Arabic one. Italians used gelatine glue and worked strongly the rags in order to get individual fibres without threads on the surface of the paper, therefore its fibres appear with shredded edges. In the course of time, other components were added to the cellulose such

Table 1: Analyzed samples

Number	Condition of paper	Date of origin	pH of ink	pH of paper
1	Italian	1360	6.8	7.2
2	acidic	1583	2.8	3.5
3	acidic	s. XVI	4.5	4.8
4	acidic	1576	3.9	4.1
5	Arabian acidic	1290	*	3.8
6	microbiological	s. XVIII	*	7.1
7	microbiological	1690	*	5.8
8	microbiological	s. XV	*	7.6
9	Italian	1360	6.5	7.2
10	low acidity	s. XVIII	*	5.8
11	low acidity	1712	6.1	6.7

* Sample without ink

SAMPLES

Manuscripts tested in this assay have been chosen according to their composition, antiquity and acidic behaviour. Infrared analysis was focused to get information about cellulose oxidative condition as well as to know how acid hydrolysis affects the cellulose chain.

The acidity of the sample is related to the corrosion power of iron gall ink against cellulose, but microbiological degradation also affects the cellulose and acidity is tested in very degraded samples.

Table 1 shows the list of samples analyzed.

EXPERIMENTAL

Apparatus

Two infrared spectrometers were used: Bomem MB-120 and Bomem DA.3. Both systems have a Glowbar source and a KBr beamsplitter. The MB-120 instrument has a triglycine sulphate (TGS) detector, beamcondenser and Spectra-Tech IR Plan Microscope, which has an MCT detector refrigerated with liquid nitrogen and an ATR objective of ZnSe. The DA.3 instrument also has an MCT detector and can be used in vacuum mode. Infrared spectra were measured at a resolution of 4 cm^{-1} in the range of 4000 to 350 cm^{-1} and 50 to 200 scans were taken in order to obtain an appropriate signal-to-noise ratio. The spectral data were processed with the GRAM/386 program.

Sample handling

Different methods were used for the analysis of paper and inks: KBr pellets, diamond cell using the microscope in transmission mode, diamond cell using the beam condenser, microscope with the attenuated total reflectance (ATR) objective and diffuse reflection (DRIFT).

KBr pellet method consists of diluting the sample in a previously dried amount of KBr, mixing and grinding in an agate mortar. The mixture is prepared about 1:100 in KBr. A pellet of 13 mm in diameter is obtained after pressing the sample. Pellets are measured in transmission mode. The diamond cell method consists of placing a small particle or fibre of sample in the middle of a diamond window and pressing it against another window. It allows an increase in the surface area of the sample and a decrease in thickness, in such a way that a beam of light can pass through and the spectra of the solid can be measured by transmission. This procedure allows the analysis of very small particles. If the spread sample occupies the whole window (about 2 mm) it is possible to use the beamcondenser of the MB-120 system. If the sample occupies only a small area, then it is necessary to use the microscope, which allows the measurement of samples as small as 10 micrometers. In case of fibres with ink it is possible to select and focalize the desired area with or without ink.

Another option of the microscope is to use the ATR objective. This is specially useful when the sample is either too thick or can not be destroyed, separated or manipulated. The ZnSe crystal of the objective is pressed against the sample and a single reflection penetrates slightly on the sample.

When the sample is big enough and it is not necessary to focalize small areas, it is possible to use the diffuse reflectance measure (DRIFT). This accessory gives us the information of the whole surface. All methodologies have been compared.

RESULTS AND DISCUSSION

Comparisons of spectral information with pH of paper allow us to see some differences in peaks when the pH changes. One of the bands which clearly increases with the pH is at 875 cm^{-1}. Although some authors[8] have assigned this band to CH_2 (swing) of the CH_2–OH present in the cellulose, we have found strong correlation with another band at 1790 cm^{-1}. Both bands are typical of the spectrum of calcium carbonate. Unfortunately another band which appears in the calcium carbonate spectrum, at 1420 cm^{-1}, can not be detected because of interferences of cellulose. Figures 5 and 6 show some spectra of papers at different pH. Samples which show a relatively strong band at 875 cm^{-1} have also shown a

big presence of calcium when they have been analysed using SEM-EDX (Scanning Electron Microscopy and X-Ray Microanalysis).

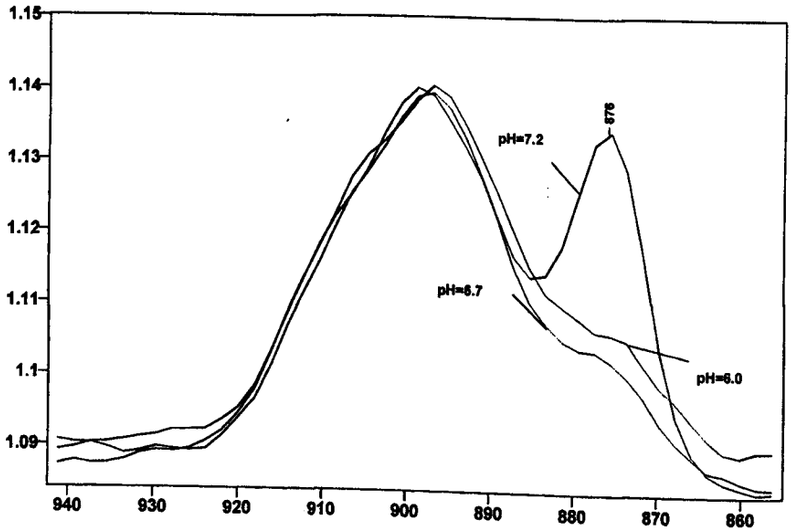

Fig. 5: Infrared spectra of the carbonate band at 876 cm^{-1} at different pH.

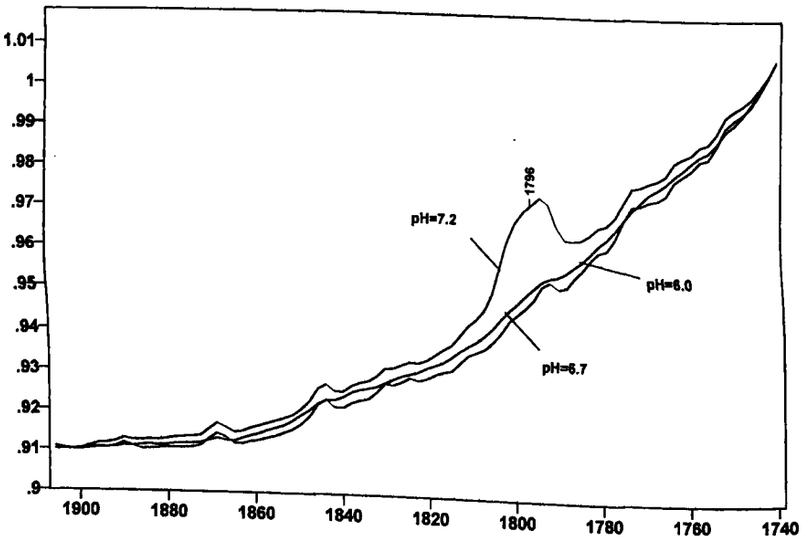

Fig. 6: Infrared spectra of the carbonate band at 1796 cm^{-1} at different pH.

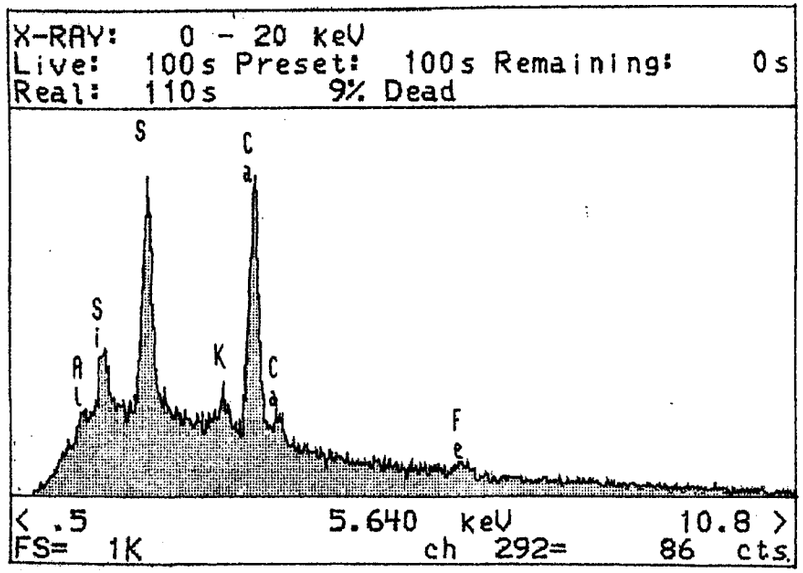

Fig. 7: SEM-EDX spectrum of calcium sulphate particles between the fibres.

Ancient papers from early XIVth century have large amounts of calcium carbonate deposited among the fibres. These samples were also analysed by SEM-EDX and this technique allows to see small particles settled in the paper which were identified as calcium from calcium carbonate. Samples with acidic pH (3–5) caused by acidic iron gall ink show sulphur and calcium peaks together in the particles (Fig. 7). This is probably due to a change from calcium carbonate to calcium sulphate because of the reaction of sulphuric acid from ink with calcium carbonate. Unfortunately, correlation between the increase of calcium sulphate and the decrease of calcium carbonate can not be corroborated by IR analysis since one of the strongest bands of calcium sulphate, that appears at 1145 cm^{-1}, interferes with cellulose. Nevertheless, this correlation was tested by SEM-EDX.

When cellulose oxidation rises in acidic samples, another characteristic band appears at 1720 cm^{-1} and changes according to pH. This band increases with decreasing pH (Fig. 8). Although this is not a neat band, but a shoulder near the water absorption, it can be detected clearly. This shoulder belongs to the C–O bond and can be explained by hydrolysis and oxidation of cellulose. The corrosive ink (iron ions and sulphuric acid) attacks the cellulose and the paper becomes acidic, therefore hydroxyl groups are oxidized to carbonyl and carboxylic groups, increasing the band.

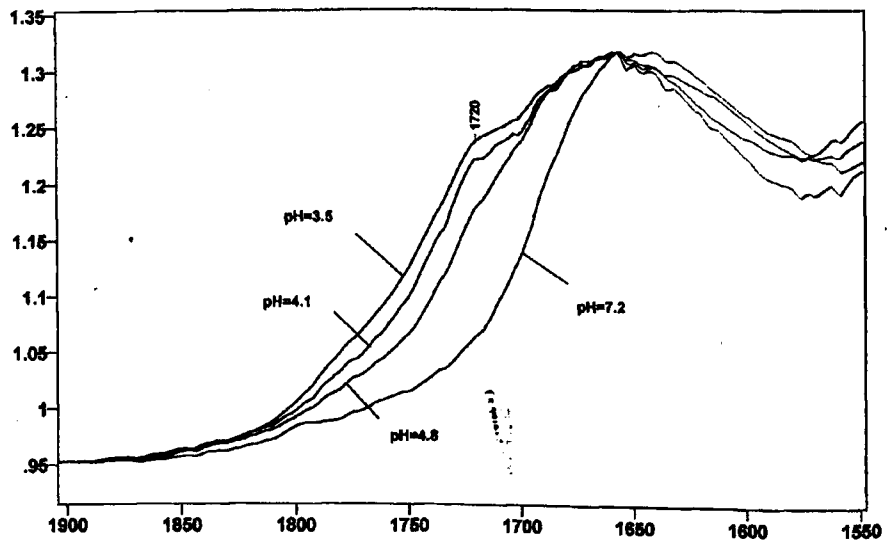

Fig. 8: Infrared spectra of C–O band at different pH.

An increase of pH is also associated to an increase of the band situated at 3430 cm^{-1} that corresponds to –OH absorption (Fig. 9). Alkaline pH contributes to keep OH-groups. Cellulose oxidation is related to acidity in degraded samples. The same cellulose oxidation reaction of O–H (hydroxyl) to C–O (carbonyl or carboxylic groups) occurs when the sample is acidic due to the corrosive ink. In addition, the hydration capacity of cellulose and H-bonds changes if this molecule is oxidized . This was also corroborated by IR analysis.

The same spectral changes can be found when the samples are analyzed using the diamond cell. The quality of spectra is worst due to the fact that the beamcondenser used with the diamond cell is in the Bomem MB-120 system, which does not allow the measurements in vacuum mode. Diffuse reflexion accessory is adapted to the Bomem DA.3 system and therefore it is possible to work in vacuum, which produces results in less noise.

All the methods used in this study: diamond cell with microscope or beamcondenser, KBr pellets, diffuse reflectance and ATR microscopy, give the same information and are equally useful for all samples analysed. There are only a couple of differences which need to be remarked. The first one is a loss of information corresponding to a small range of the spectra, below 750 cm^{-1},when using the microscope, due to the narrow range response of the MCT detector. The second one is the bad quality of spectra when non-degraded samples are measured with ATR microscope. This is probably due to the possibility of testing touch a

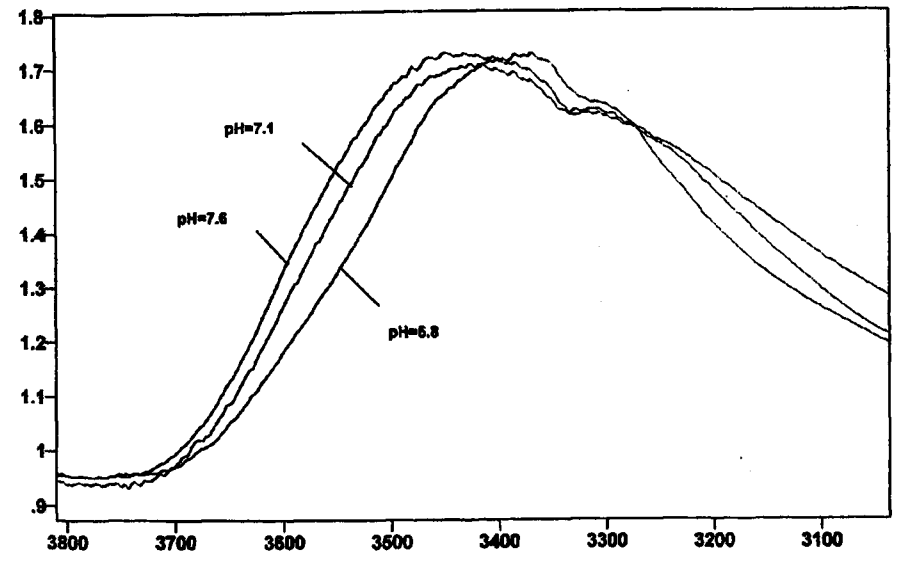

Fig 9: Infrared spectra of O–H band at different pH.

zone without fibres when the ATR objective is pressed against the surface of the sample. In degraded samples, the probability to find even a shredded fibre is higher.

CONCLUSION

Fourier transform infrared spectroscopy allows rapid analysis of samples of paper without previous treatment.

Even if only a small amount of sample is available, which happens in samples from museums and archives, the infrared technique allows us to use a beamcondenser or a microscope. When samples can not be altered at all, the ATR objective of the microscope allows to measure on the surface of paper without removing any fibre. Only in samples where fibres are not degraded, the last methodology shows some limitations in the quality of spectra.

Cellulose oxidation and dehydration can be tested in acidic samples from manuscripts degraded by microbiological agents or by corrosive irongall ink. Characteristic C–O band increases in acidic samples and hydration capacity of cellulose decreases. Both results certify degradation in cellulose.

Non acidic papers have large amounts of calcium carbonate, which was tested by FTIR and SEM-EDX. It has been observed that in acidic papers from later centuries, there is a change from calcium carbonate to calcium sulphate caused by ink.

FTIR combined with other analytical techniques such as SEM-EDX can be very useful to analyze and evaluate degradation in manuscripts.

ACKNOWLEDGEMENTS

The analysis of fibres by SEM-EDX were performed at the Electron Microscopy Section of the Scientific Technical Services of the University of Barcelona. We acknowledge Dr. R. Fontarnau and coworkers for their contribution.

SUMMARIES

Fourier transform infrared spectroscopy applied to the analysis of ancient manuscripts

Fourier transform infrared spectroscopy has been applied to the characterization of manuscript degradation. Samples were small pieces or individual fibres from paper manuscripts that dated from 1360 to the end of the eighteenth century. The pH at the surface ranged from 4 to 7.6 due to irongall ink corrosion or biological degradation.

Several IR techniques were tested in order to choose the best, considering the condition of the sample and the need to minimize the damage: KBr pellets, diamond cell using the microscope in transmission mode and diamond cell using the beam condenser, microscope using the attenuated total reflectance (ATR) objective and diffuse reflexion (DRIFT) were compared.

Variations of O–H and C–O absorptions show the degree of cellulose oxidation. More degraded samples show more intense C–O bands and weaker O–H bands.

Using this method it is also possible to measure carbonate bands, which are stronger when paper is in a good condition and not degraded.

Manuscript degradation depends on the acidity of irongall inks and alkaline buffering of the paper. A decrease in alkaline buffering in degraded samples analyzed by SEM-EDX corroborates the measurements of carbonates obtained by infrared analysis.

La spectroscopie infrarouge par transformation de Fourier appliquée à l'analyse de manuscrits anciens

La spectroscopie infrarouge par transformation de Fourier a été appliquée pour déterminer l'état de dégradation de manuscrits. Les échantillons utilisés étaient des petits morceaux ou des fibres individuelles de papier émanant de manuscrits datant de 1360 jusqu'à la fin du 18ème Siècle. Le pH à leur surface varie entre 4 et 7,6 selon le degré de corrosion de l'encre gallique ferrée ou selon la dégradation biologique.

Différentes techniques infrarouges ont été testées afin de pouvoir sélectionner la plus adaptée à l'état de l'échantillon et de minimiser le risque d'endommagment de celui-ci: on a utilisé des boulettes de bromure de potassium, une cellule de diamant utilisant le microscope en mode de transmission et une cellule de diamant utilisant un condenseur de rayon, un microscope utilisant un objectif à réflexion totale atténuée (ATR) ou à réflexion diffuse (DRIFT) et on a comparé les résultats.

Les variations dans l'absorption de O-H et C-O mettent en évidence le degré d'oxydation de la cellulose. Les échantillons plus dégradés présentent des liaisons C-O plus intenses et des liaisons O-H plus faibles.

Cette méthode permet également de mesurer les liaisons de carbonate qui sont plus fortes lorsque le papier est en bon état et pas dégradé.

La dégradation d'un manuscrit dépend du degré d'acidité de l'encre gallique ferrée et de la présence de tampon alcalin dans le papier. Une diminution du tampon alcalin dans les échantillons dégradés, mise en évidence par l'analyse SEM-EDX, confirme les mesures de carbonate obtenues par l'analyse infrarouge.

Die Anwendung der Fourier-Transformations-Infrarot-Spektroskopie bei der Untersuchung historischer Handschriften

Die Fourier-Transformations-Infrarot-Spektroskopie wurde zur Erfassung des Abbauzustandes von Handschriften eingesetzt. Untersucht wurden kleine Stücke bzw. einzelne Fasern von Papierhandschriften aus der Zeit zwischen 1360 und dem Ende des 18. Jahrhunderts. Ihr Oberflächen-pH lag zwischen 4 und 7,6, ersteres als Folge von Tintenfraß oder biologischem Abbau.

Verschiedene Infrarot-Techniken wurden auf ihre Eignung getestet, wobei es vor allem um den Zustand der Proben und die Notwendigkeit ging, eine Beschädigung derselben zu minimieren: Kaliumbromid-Preßlinge, Diamantzelle unter Verwendung des Mikroskops in Transmissionsmodus, Diamantzelle mit einem Strahlenkondensor, Mikroskop mit abgeschwächtem Totalreflexionsobjektiv (ATR) und mit diffuser Reflexion (DRIFT) wurden verglichen.

Unterschiede in der Absorption von O–H und C–O zeigen den Oxidationsgrad der Cellulose auf. Stärker abgebaute Proben weisen intensivere C–O- und schwächere O–H-Banden auf.

Die Methode ermöglicht auch eine Messung der Carbonat-Banden; diese sind stärker bei festen, nicht abgebautem Papier.

Der Abbauzustand von Handschriften hängt vom Säuregrad der Eisengallustinte und vom Vorhandensein eines alkalischen Puffers ab. Ein Rückgang der alkalischen Pufferung in abgebauten Proben, nachgewiesen durch REM-EDX, bestätigt Carbonat-Messungen mittels Infrarot-Analyse.

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The Effect of Aqueous Solutions of Alkoxypolyethyleneglycols (ALKPG) on the Mechanical Properties of Paper

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INTRODUCTION

The principal cause of paper degradation in libraries is acid-catalyzed cellulose hydrolysis in paper fibers. Paper deacidification reduces degradation rates, and it has been proven that lifespan of deacidified papers is 3 to 5 times greater than that of untreated acid papers[1,2].

DEACIDIFICATION TREATMENTS

Aqueous deacidification treatments, based on single sheet immersion in aqueous magnesium or calcium bicarbonate solutions[3], remain the surest and most appropriate methods for restoration of old valuable books and documents, though they have been used also for newspapers mass treatment (Vienna method). Water wetted paper is very weak and severe deformations occur during drying, so use of non-swelling organic solvents has been tried since the sixties and seventies. Hydrocarbons (flammable) and alkyl halides (non flammable) solvents have been used: their low surface tension and viscosity allow a quick wetting and impregnation of paper, and in addition they are poor solvents to inks, glues and other components of books, allowing only minimal changes to the original state. Therefore, the research was directed to find magnesium and calcium compounds, of alkaline nature, that were soluble in such non polar solvents. The choices are not very wide.

NON-AQUEOUS METHODS

R.D. Smith[1] first introduced deacidification solutions of magnesium alkoxides $(RO)_2Mg$ in chlorofluorocarbons (CFC). These solutions were unstable in moist air without the presence of alcohols as cosolvents. Later, it was found that CFC solutions of carbonated magnesium alkoxides $(RO)_2Mg.(CO_2)_x$ are more stable and need less alcohol as cosolvent. The last ones can be applied by immersion in vacuum closed systems (methods Wei t'o and Sablé) and in spray (local treatments). CFC compounds, after their prohibition in Montreal protocol, have to be replaced by other halogenated hydrocarbons not (or less) ozone depleting, for instance HFC and FC (method FMC)[4,5], that do not contain chlorine, or by other families of solvents, like saturated hydrocarbons or silicones (method Battelle)[6]. These replacements are complicated, because design of mass deacidification systems is tightly restricted by physical and thermodynamic properties of the solvents used. Furthermore, CFC substitutes are quite more expensive.

Methoxymagnesium methylcarbonate (MMC), $(CH_3O)_2Mg(CO_2)_x$, the substance used in Wei t'o method, is an extremely moisture-sensitive compound, which must be always used in diluted solution. Reaction with atmospheric water vapour and carbon dioxide leaves on the paper, as main end-product, magnesium basic carbonate, stable compound of formula $Mg(OH)_2 \cdot [MgCO_3]_4 \cdot 5H_2O$. This means that after complete solvent evaporation, the paper has got an alkaline reserve similar in nature to that deposited on the same paper deacidified with a magnesium bicarbonate solution. Another advantage is the absence of swelling and dimensional changes, but usually ca. 30% of the books in a collection cannot be treated, in order to prevent deterioration of some inks, colours and plastic covers.

Gas-phase deacidification methods have given diverse results: The first gas used was ammonia (Bavarian State Library, 1950), then amines such as cyclohexylamine carbonate (Langwell, 1975), what was abandoned when it was classified as carcinogen, and ethanolamines (reaction between gaseous ammonia and ethylene oxide on the paper, in situ). The most elaborated method uses diethylzinc (DEZ)[7] as gaseous reactant. US Library of Congress has tested and applied this method for a long time (1974–1994), until finally another completely different method is preferred, the said solid Bookkeper method[8], which applies magnesium oxide microparticles on the paper, from a suspension in a perfluorocarbon.

Every mass deacidification treatment now available has its pros and cons. Research in this field is far to come to an end, and many efforts still should be made to find a treatment close to the ideal one, that is, efficient, permanent, and independent of bibliographic substrate.

Table 1: Chemical description of alkoxy polyethyleneglycols

	Butoxytriglycol (BTG) Butylglycol	Methoxypolyethylene-glycol 350 (MPG)
Chemical name	Poly(ethyleneglycol)butyl ether [9004-77-7]	Poly(ethyleneglycol)-methyl ether [9004-74-4]
Formula	$CH_3(CH_2)_3(OCH_2\text{-}CH_2)_n OH$ n≈3	$CH_3O(CH_2\text{-}CH_2O)_nH$ n≈7,3
Refractive index (n_D^{20})	1,4400	1,4550
Density (d)	0,990	1,094
Flash point (Fp)	>110°C	
Melting point (Tm)		-8° C
Library of FT-IR-Spectra		1(2),1172A
Library of Regulatory & Safety Data (R&S) reference		(2),3157G
Beilstein reference	1(4),2402	
Structure Index reference (SI)	499,B1	499,A1
Risk Index ref. (R)	20/21/22-36/37/38	
Safety Recommendation ref. (S)	26-36	
Molecular weight (M); average	ca. 206	ca. 350
Lib. of Chem. Safety Data ref.		2,2872D
Register of Toxic Effects of Chem. Substances ref. (RTECS)		#PE8263000
State	liquid	
Solubility	water soluble	
Viscosity (100° C):		4,1 cStokes

Table 2: Mass deacidification agents

Chemical name	magnesium butoxy triglycolate, carbonated	magnesium methoxy polyethylene glycolate, carbonated
Formula	$Mg(BTG)_2(CO_2)_x$ x≈1	$Mg(MPG)_2(CO_2)_x$ x≈1
Chemical structure	$^{-}O\text{-}CH_2\text{-}(O\text{-}CH_2\text{-}CH_2)_3\text{-}CH_2\text{-}CH_2\text{-}CH_3$ ^{++}Mg $^{-}OOC\text{-}O\text{-}CH_2\text{-}(O\text{-}CH_2\text{-}CH_2)_3\text{-}CH_2\text{-}CH_2\text{-}CH_3$	
Magnesium content	5,0%	3,1%
M; average	478	766
State	semi-solid, waxy; moisture sensitive	
Solubility	soluble in non-polar solvents: freon, alkyl halides, aromatic and aliphatic hydrocarbons, etc	
Hydrolysis	$[C_4H_9(OCH_2CH_2)_3O]_2MgCO_2 + H_2O \rightarrow 2\ C_4H_9(OCH_2CH_2)_3OH + x\ Mg(OH)_2 + y\ MgCO_3$	

ORGANIC COMPOUNDS OF NON-AQUEOUS LIQUID TREATMENT

Carbonated magnesium alkoxypolyalkoxides[5], compounds derived from alkoxypolyethylenglycols (ALKPG), that is, non-volatile primary alcohols of high molecular weight, do not need the presence of alcohols for a complete dissolution in organic non polar solvents, as aliphatic or aromatic hydrocarbons or alkyl halides (cf. Table 1). Concentrated viscous solutions obtained can be freely diluted and easily carried towards the treatment chamber by means of vacuum, where books are impregnated, with less risk of damage to bindings and inks, but difficulty is encountered in penetrating thick volumes, even applying high pressures. Furthermore, and due to the reduced magnesium content per molecule, a great amount of substance is needed to reach a sufficient alkaline reserve (1% as $MgCO_3$), and as a result a waxy and heavy residue is left on the paper.

ALKOXY POLYETHYLENE GLYCOLS

The main goal of this work is to study the effects of alkoxypolyethyleneglycols on the mechanical properties of paper, in order to predict the effects of carbonated magnesium alkoxypolyalkoxides. It is difficult to carry out a systematic study of the effects of said compounds, using the pilot plant of our laboratory, because of space and time requirements, so we decided to apply separately on the paper the polyglycols and the magnesium salts, i.e. their hydrolitic products, in form of aqueous solutions.

The work hypothesis is that a deacidified paper, after removal from a mass treatment chamber, when left in contact with moist air for a long time, becomes impregnated by an organic substance, the alkoxypolyethyleneglycol, and covered by an inorganic deposit, the magnesium basic carbonate. The desirable deacidification has been achieved, but the secondary effects on the paper's mechanical strength need to be known in order to set up the optimum amount of reagent.

The method used in this study consists in measuring and evaluating the changes produced in the dimensional and mechanical properties of paper by different amounts of two selected alkoxy polyethylene glycols, applied by impregnation with their aqueous solutions. Papers have been also treated with magnesium bicarbonate solutions[9], at different concentrations, and tested by the same procedures. The following paper characteristics have been determined before and after said impregnations:

- Thickness
- Grammage
- Breaking length
- Tensile Energy Absorption

- Tensile strength
- Stretch at break
- Modulus of elasticity
- Folding endurance

All the tests have been carried out with the same modern paper, a commercial brand for photocopying, of a unique lot. We did not intend to evaluate neither paper or treatment permanence, so that the tests have not been repeated after artificial ageing.

In order to explain reasonably the results found, there have been used two relatively simple theories about paper structure: the molecular theory for the elasticity of paper, which derives Young's modulus from the number and density of hydrogen bonds in cellulose[10-15], and the theory of liquid sorption by paper, which considers paper as a system of pores and fibers, with different reactivity to polar or non-polar liquids[16].

EXPERIMENTAL

Materials and chemicals

- Paper for photocopying and ink jet printing (*Inapa Multioffice* brand), of 80 g/m^2 grammage, handled as 210 mm x 297 mm x 0,11 mm DIN A4 pages.
- Butylpolyglykol (also known as Butoxypolyethyleneglycol or Polyethyleneglycolmonobutylether) from Hoechst Ibérica, S.A.
- Methoxypolyglykol M350 (also named as Methoxypolyethyleneglycol 350) from Hoechst Ibérica, S.A.
- Magnesium basic carbonate: $Mg(OH)_2 \cdot [MgCO_3]_4 \cdot 5H_2O$, from Merck.
- Carbon dioxide, from Carburos Metálicos, S.A.

Preparation of treatment baths

- Butylglycol (BTG) and methoxypolyglycol (MPG) solutions:
  Volume: 3000 cm^3
  Concentrations(% w/w): 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 in distilled water.
  The corresponding molar concentrations are given in Table 3.
- Magnesium bicarbonate solution[3,17]:
  4 g of magnesium basic carbonate are dispersed per liter of water. Then a CO_2 stream is bubbled through the suspension until the solution becomes

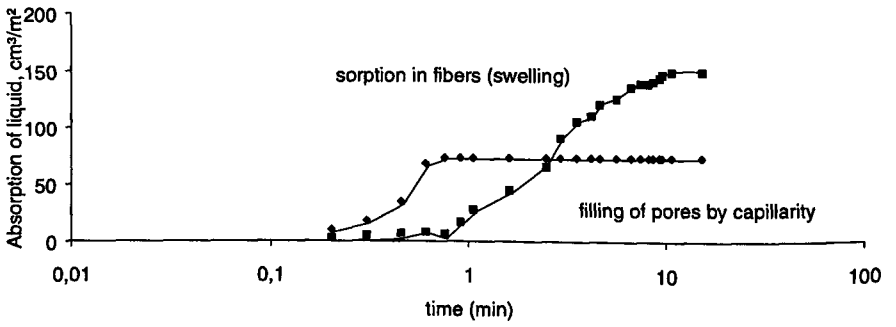


Fig. 1: Sorption of liquids by paper (photocopy paper, 80g/m²). Curve ◆: sorption of a non-polar liquid (oil); quick pore filling by capillarity, no fibre swelling. Curve ■: sorption of water; slow fibre swelling, then pore filling.

clear. The concentration of the saturated solution is 0,052 M $Mg(HCO_3)_2$. By subsequent dilutions of convenient volumes of the saturated solution up to one liter of solution with distilled water, the following concentrations (% w/w) are prepared: 0.25, 0.5, 0.75, 1, 1.5, 2.
Corresponding molar concentrations are given in Table 3.

- Impregnation procedure
  A block of 4 DIN A4 paper sheets, separated each other by a sheet of non-woven PP textile, and supported by 2 PP mesh, is held horizontally with both hands and immersed in the bath, without making any stress on the plane of the paper. Sized paper needs to be dipped for 15 min for a complete wetting (cf. Fig.1). Then the block is taken off the bath, letting the excess water drain off by hanging it vertically, and then it is let dry at room temperature on a horizontal rack. After 24 h, the dried sheets are separated and stored in a temperature and humidity controlled room, at 23° C ± 1 and 50% RH ± 3, until they reach the moisture equilibrium with air; normally a period of 48 h or more is needed for it. All the subsequent tests are made under the same standard atmospheric conditions.

Equipment

- Tensile test machine (electronic dynamometer, linked with the computer), model Proteo, made by Investigación Sistemas Papeleros, S.L. (I.S.P.), Oiartzun, Spain.
- Folding endurance test machine, made by I.S.P.

Table 3: Mechanical strength numbers of photocopy paper 80 g/m² before and after treatment

Concentration		Breaking load N		Strech at break %		Tensile energy absorption J/m²		Breaking length km		Elastic limit N		Strech at elastic limit %		Folding endurance n	
%	mol/l	MD	CD	MD	CD	MD	CD	MD	CD	MD	CD	MD	CD	MD	CD
untreated		83,3	37,1	1,98	5,50	101,5	125,3	7,55	3,19	37,6	15,6	0,78	0,9	299	89
water only		68,2	31,3	2,52	6,31	76,4	93,1	6,59	2,66	23,4	13,4	0,74	1,0	246	107
butoxy triglycol (BTG)															
0,5	0,024	64,4	31,2	2,36	5,72	74,5	90,2								80
1	0,049	60,7	31,0	2,20	5,13	91,6	108,2							161	53
2	0,097	60,8	29,1	2,20	4,26	91,7	98,0							163	37
3	0,146	53,6	28,0	2,20	4,05	80,9	93,0							150	53
4	0,194	51,1	27,2	2,08	4,43	73,4	86,0							138	27
5	0,243	47,1	25,1	1,84	4,85	60,8	83,3							110	26
6	0,291	45,4	24,8	1,66	4,28	53,1	73,1							67	23
7	0,340	42,4	25,1	1,84	4,60	54,6	78,4							48	12
8	0,388	38,8	22,4	1,55	3,55	42,6	54,7							32	11
9	0,437	38,7	20,7	1,60	3,74	43,8	50,0							24	9
10	0,485	34,0	18,1	1,53	3,14	36,3	42,0							15	9
metoxy polyethylene glycol (MPG)															
0,5	0,014	76,4	29,8	2,56	6,50	74,4	90,2	6,49	2,53	25,9	12,4	0,70	0,9	384	156
1	0,029	70,0	33,5	2,63	6,00	71,5	94,1	5,95	2,85	25,6	13,9	0,72	0,9	240	124
2	0,057	64,3	31,65	2,70	5,85	65,6	86,7	5,46	2,69	26,1	13,5	0,82	0,9	217	
3	0,086	66,5	29,8	2,49	5,70	58,8	79,4	5,71	2,53	27,3	13,1	0,80	0,9	151	51
4	0,114	55,7	29,65	2,42	5,40	52,4	75,0	4,73	2,52	23,1	12,95	0,75	0,9	134	
5	0,143	50,3	29,5	2,07	5,10	38,2	70,6	4,19	2,50	21,2	12,8	0,76	0,9	94	74
6	0,171	60,3	23,2	2,61	4,85	61,3	53,4	5,12	1,97	21,9	10,95	0,70	1	112	
7	0,200	55,6	16,9	2,16	4,60	46,1	36,3	4,72	1,44	22,1	9,1	0,72	1,1	53	12
8	0,229	47,1		2,21		39,2		3,97		19,6		0,70		30	
9	0,257	54,7		2,35		48,5		4,65		20,3		0,69		82	
10	0,286	33,8		1,79		21,5		2,79		17,8		0,79		16	
$Mg(HCO_3)_2$															
0,25	0,017	60,9												213	
0,5	0,034	58,9												212	
0,75	0,051	62,3												207	
1	0,068	66,0												207	
1,5	0,103	60,3												202	
2	0,137	56,8												151	

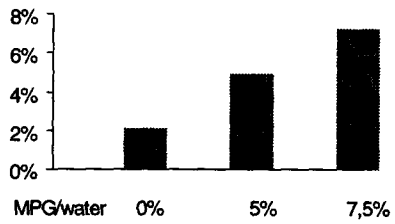


Fig. 2: Increase in grammage. Paper (67 g/m²) impregnated with MPG 350, dried and conditioned at 50% RH.

shown that samples of printing paper of 67 g/m² grammage wetted with water, MPG 5%, and MPG 7,5% solutions increase their grammage in 2,0%, 4,8% and 7,2% respectively after complete drying (4 days) in an atmosphere constantly maintained at 50% RH. This can be attributed not only to the MPG absorbed, but also to some additional water retained by the MPG. No determination of absolute moisture has been made in order to confirm this fact.

CHANGES IN MECHANICAL PROPERTIES

Plots of each mechanical property against solute concentration in weight percent, both in machine direction and cross direction, give indications about the influence of each substance. As an example, Fig. 3 and 4 show the decreasing of breaking force and folding endurance due to impregnation with BTG and MPG. Graphs for the other parameters are similar.

Method for comparing the effects of the three chemicals

This comparison is only possible by relating all the determined changes against a unique concentration scale. Thus, practical concentration in weight percent has been converted in molar concentration, and arithmetic mean values of the different mechanical characteristics have been correlated with concentration, using in all the cases, the method of linear regression. This method may be discussed, because in some cases perhaps a polynomical regression could be better, but linear regression is useful enough to find the main tendency, especially when few experimental data are available. Table 4 shows the values of all the correlation coefficients obtained, together with the slopes of the straight lines and ordinates at the origin. Note that every slope is negative, showing that a reduction is always produced, that means, paper tends to weaken in all the cases.

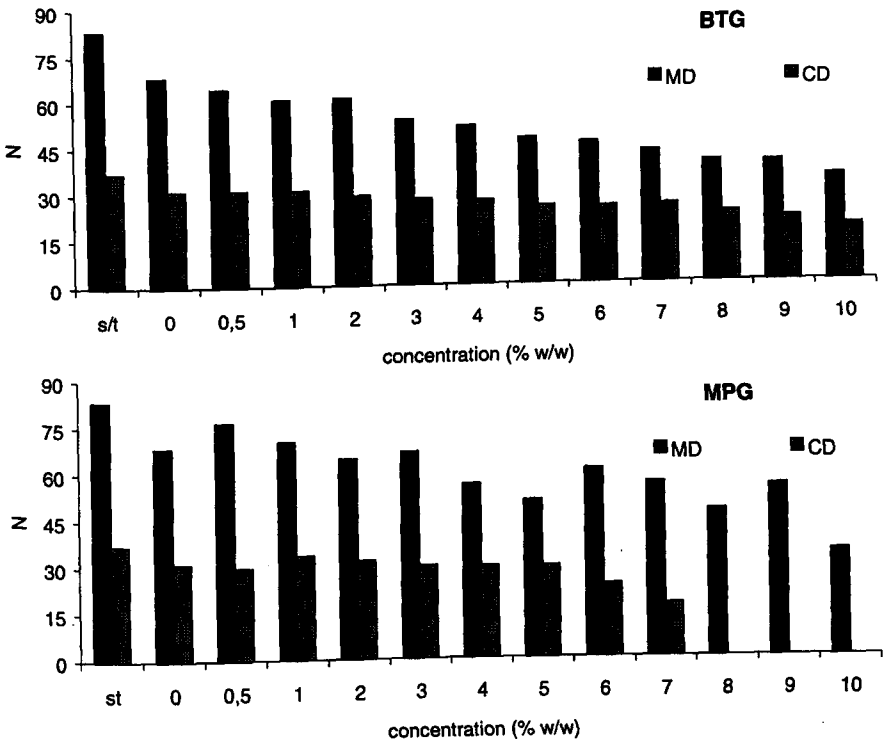


Fig. 3: Breaking load of paper (80g/m²) treated with ALKPG solutions.

Table 4: Values of r^2, a and b for the regression straight lines. Y = aX + b (Y=mechanical property, X=molar concentration)

		Breaking load		Stretch at break		Tensile energy absorption			Breaking length		Folding endurance	
		MD	CD	MD	CD	MD	CD	√(MD*CD)	MD	CD	MD	CD
BTG	r^2	0,98	0,97	0,92	0,68	0,83	0,85	0,86			0,95	0,77
	a	-66	-25	-2	-4,5	-105	-114	-109			-445	-164
	b	65,3	31,9	2,4	5,52	88,5	105	96,2			213	74
MPG	r^2	0,76	0,66	0,55	0,97	0,83	0,90	0,95	0,75	0,69	0,80	0,77
	a	-104	-59	-2	-9	-160	-260	-208	-9,64	-5,6	-988	-564
	b	72,3	33,7	2,64	6,4	74,7	98,9	86,0	6,29	2,95	277	129
$Mg(HCO_3)_2$	r^2	0,35									0,80	
	a	-49									-518	
	b	64,8									236	

PHYSICAL TESTS

Tensile test

Tensile test was performed according to standardized methods[18,20], on test specimens of 15 mm 210 mm, distance between clamps 180 mm, constant rate of separation of clamps 100 mm/min. Following values are provided directly by the testing machine: breaking force (N), stretch at break (%), elastic limit (N), stretch at elastic limit (%), breaking length (km) and tensile energy absorption (J/m^2). Tensile strength values are calculated dividing the breaking force by the test specimen width (15 mm), and modulus of elasticity is obtained from elastic limit, stretch at elastic limit, and thickness (constant value 0,109 mm).

The test is repeated at least 10 times in the two main perpendicular directions, longitudinal (machine; MD) and transversal (cross machine; CD). For the determination of Young's modulus in the MD direction, the stretching speed was lowered down to 20 or 50 mm/min, because at higher speeds, some elastic limit values could not be recorded in the computer.

In all the stress-strain graphs a short delay in the strain axis could be observed, from the initial point up to the first stress registered. This "dead strain" of about 0,36% in all the specimens, has been substracted from the stretch at elastic limit, in order to calculate more accurately the Young's modulus.

Folding endurance test

The number of double folds until the failure of the test specimen clamped under a constant load is measured according to standardized methods[21,22]. A minimum number of 20 test specimens cut in machine and cross direction are used. The test specimen dimensions are 15 mm x 210 mm, and strip length between clamps is 150 mm. An exact load of 1000 g is applied to both ends of the paper strip during the test.

RESULTS AND DISCUSSION

Changes in thickness

Sorption of water, aqueous solutions and water-like liquids causes swelling of paper[16]. This is shown by comparing the thickness of dry sheets untreated and treated with water, 5% MPG and 7,5% MPG. Thickness is measured with a caliper, placing a block of sheets between two glass plates. Thickness measurements are made also in the paper during drying, until moisture equilibrium is attained.

Sheet thickness increases with polyglycol concentration. For example, samples of printing paper of 67 g/m^2 grammage wetted with water, MPG 5%, and MPG 7,5% solutions show increases of thickness of 5,1%, 7,0% and 8,7% respectively after complete drying at an atmosphere of 50% RH. Elasticity modulus is influenced by thickness changes. In this study all moduli values have been calculated using the same initial thickness, considered constant. If actual thickness values had been used, even lower modulus values would be obtained.

Swelling of cellulose

Cellulose swells in different solvents[16,37]. The extent of swelling depends on the solvent as well as on the nature of the cellulose sample. In the case of native cellulose with fibrous structure more or less drastic morphological changes take place depending on whether the swelling is interfibrillar or intrafibrillar. More generally, the differences caused are distinguished in terms of intercrystalline or intracrystalline swelling. In the former case the swelling agent enters only into the disordered (amorphous) regions of the cellulose microfibrils and between them, whereas in the latter case the ordered (crystalline) regions are penetrated.

When bone-dry cellulose fibers are exposed to humidity, they adsorb water and the cross section of the fibers is increased because of swelling. At a 100% relative humidity this swelling corresponds roughly to a 25% increase in the fiber diameter. An additional 25% increase in swelling takes place when the fibers are immersed in water. In the longitudinal direction the dimensional change is very small.

The water retention of cellulose fibers at a given relative humidity varies depending on whether the equilibration has taken place by desorption or adsorption (hysteresis). The water uptake also continuously decreases after repeated drying and moistening of the fibers. Additional factors influencing the ability of fibers to swell are their chemical composition, such as their hemicellulose and lignin content.

Cellulose swells in electrolyte solutions because of the penetration of hydrated ions which require more space than the water molecules.

CHANGES IN GRAMMAGE

Impregnation of paper with alkoxypolyethyleneglycols causes an increase of grammage. A simple experiment carried out in parallel with this study, has

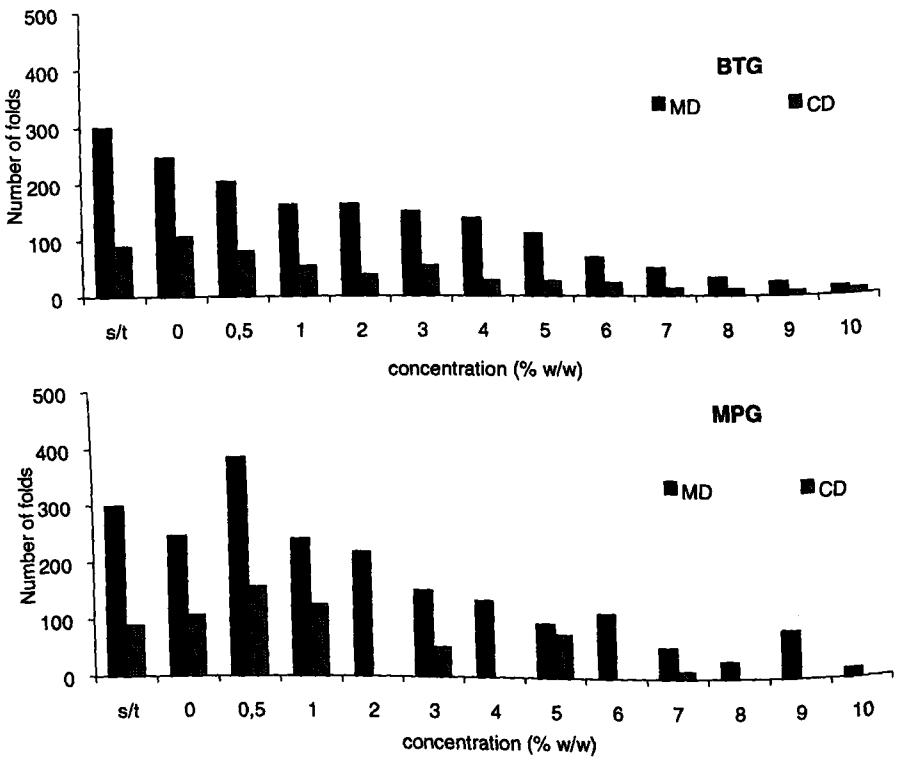


Fig. 4: Folding endurance of paper (80g/m²) treated with ALKPG solutions.

Fig. 5 to 9 show the corresponding graphs including average values and regression lines plotted against a unique concentration scale.

Changes in breaking force

The breaking force average values for the treated papers decrease gradually up to approximately the 50% of the initial values, for an alkoxypolyglycol concentration of 0,5 mol/l. This change is markedly strong in the case of MPG, which has a longer chain (n=7) in its molecule, than BTG (n=3). Changes measured in cross direction are stronger than those in machine direction.

Note that papers treated with methoxypolyglycol have been tested in cross direction up to a concentration of 7% (0,3 mol/l); for this reason comparisons with butylglycol at concentrations over this value are not reliable. Magnesium bicar-

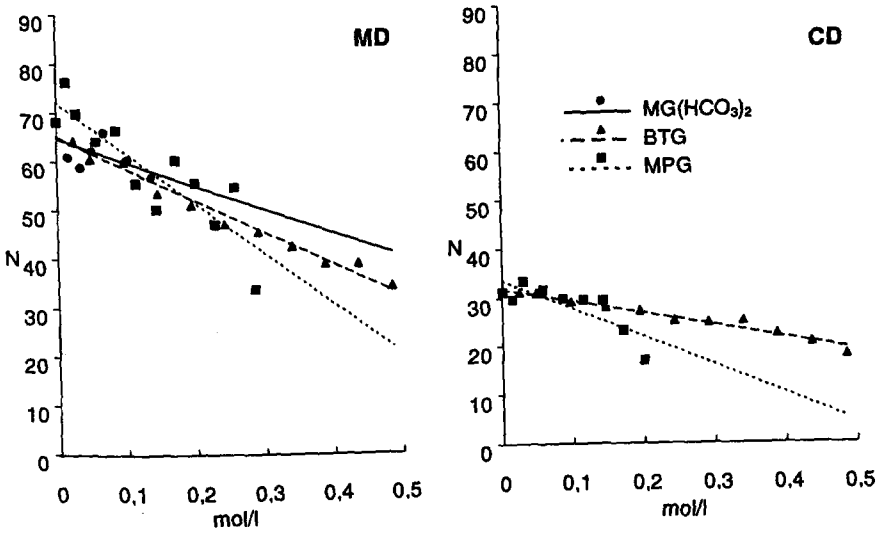


Fig. 5: Comparison of effects of $Mg(HCO_3)_2$, BTG and MPG on breaking load. A good correlation is achieved with BTG only, but trend comparison is possible.

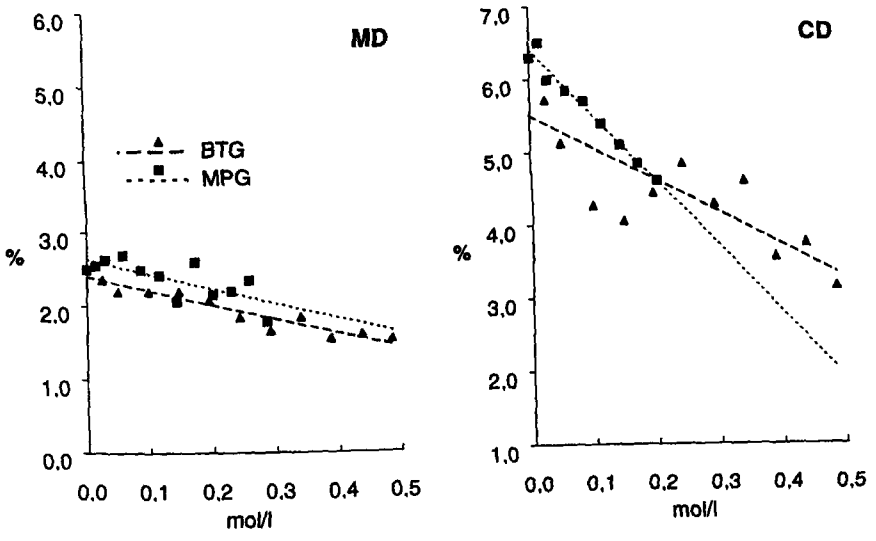


Fig. 6: Relative changes of stretch at break. In the MD plot the effect of plastification at low concentrations is observed.

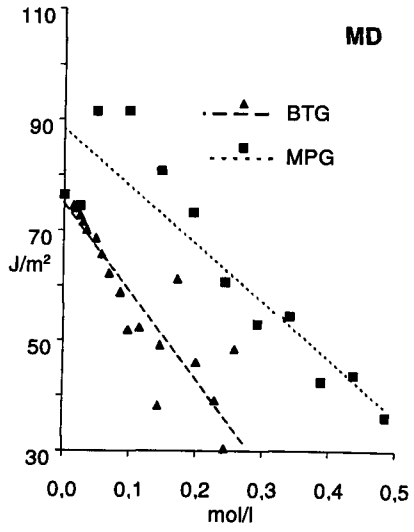


Fig.7: Comparison of of tensile energy absorption for paper impregnated with BTG and MPG. Influence of molecular size is clear.

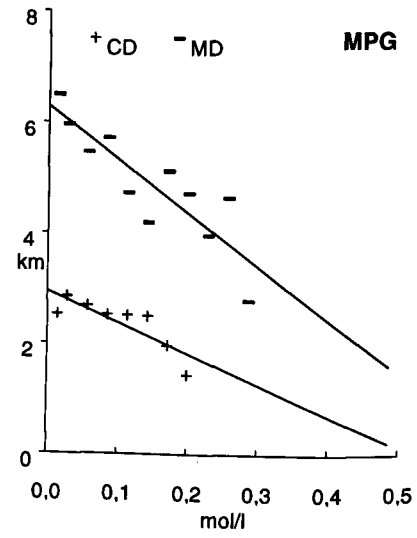


Fig. 8: Breaking length. Because of the higher grammage of impregnated paper, the values are higher than those of Fig. 5

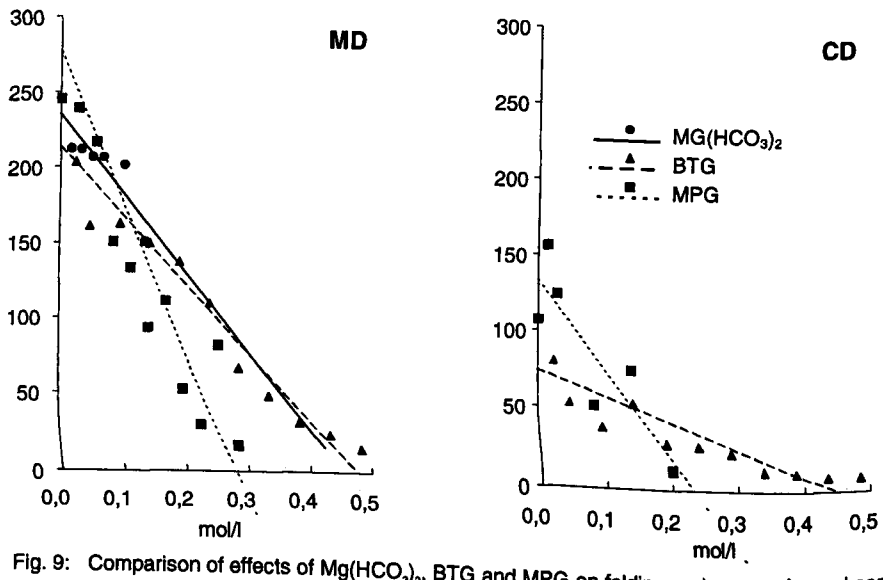


Fig. 9: Comparison of effects of $Mg(HCO_3)_2$, BTG and MPG on folding endurance. A good correlation coefficient is achieved with BTG, but trend comparison is possible. Effect of magnesium salts (MD) cannot be extrapolated to higher concentrations.

bonate diluted concentrations cause little changes in breaking force, but the results cannot be extrapolated at high concentrations, comparable to those of polyglycols.

Changes in stretch at break

Stretch at break of papers wetted with water or polyglycol diluted solutions up to 0,3 mol/l is higher than that of non wetted paper. It seems that impregnation of paper causes a slight increase in plastic behaviour, measured in machine direction. But the tendency is also negative, so at higher BTG or MPG concentration paper is weak enough to have low values of stretch at break. Here the polyglycol length influence is also relevant: paper impregnated with MPG at diluted concentrations becomes less stiff than paper wetted with BTG. In cross direction no increase of this property is observed.

Changes in breaking length

Values of breaking length, that is, the length of a strip of paper of the same width of the specimen that breaks under its own weight, are obtained by dividing the breaking load by the grammage. Grammage value used in calculating breaking length is constant, 80 g/m^2, the initial value corresponding to untreated paper at 50% RH. Therefore, changes must be exactly the same as for breaking load. But if actual values of grammage for impregnated papers had been used, even worse values would be obtained, for it has been shown that grammage increases with concentration. These values are only available for paper treated with methoxypolyglycol. No differences are observed between machine direction and cross direction.

Changes in tensile energy absorption

This mechanical quantity equals the area under the curve of the stress-strain graph. Machine direction values are similar than those calculated in cross direction, because a lower tensile strength is compensated by a higher value of elongation. Relative changes are also negative in all cases, being the loss of tensile energy more marked in the case of methoxypolyglycol, in cross direction. Comparison of geometric mean values (MD/CD) shows that MPG weakens the paper more than BTG does.

Changes in folding endurance

This test has been considered the most sensitive for detecting structural changes in paper, and has been widely used for evaluating deacidification treatments[23]. Although significant values are difficult to obtain due to the great dispersity of data, the tendencies of their changes are more marked than that of tensile values. Here even a slight increase is observed in papers treated with water and MPG diluted solutions, especially in cross direction, but the values fall down quickly as concentration increases. Regression lines cross the X-axis at 0,3 mol/l concentration in the case of MPG and 0,5 mol/l in BTG, that means, paper structure becomes completely damaged, and the paper sheet fails at the slightest bending stress. Effect of magnesium salts cannot be well distinguished from the effects of glycols, due to the lack of data at higher concentrations.

Changes in Elasticity

Elasticity of paper can be explained by the molecular theory[15,24], which derives Young's modulus from the number, density and characteristics of the hydrogen bonds in paper. The calculated results from the equations of this simple theory show a good correlation with experimental results obtained from tensile tests in the elastic regime. The calculations made and the results obtained are shown in the Appendix. Experimental moduli given in Fig. 10 and 11 are calculated from the maximum slopes of the stress-strain curves. It can be seen that polyglycols impregnating the papers also reduce elasticity of paper, and that this effect increases with molecular size.

Cellulose structure

Cellulose[25] is a homopolysaccharide composed of β-d-glucopyranose units which are linked together by (1→4)-glycosidic bonds. Cellulose molecules are completely linear and have a strong tendency to form intra and intermolecular hydrogen bonds[26,27,28,29,30]. Bundles of cellulose molecules are thus aggregated together in the form of microfibrils, in which highly ordered (crystalline) regions alternate with less ordered (amorphous) regions. Microfibrils build up into fibrils and finally cellulose fibres. As a consequence of its fibrous structure and strong hydrogen bonds[31,32,33] cellulose has a high tensile strength and is insoluble in most solvents.

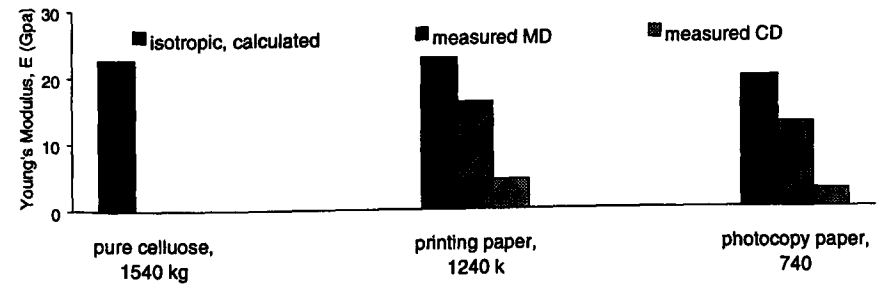


Fig. 10: Modulus of elasticity calculated and determined from tensile tests

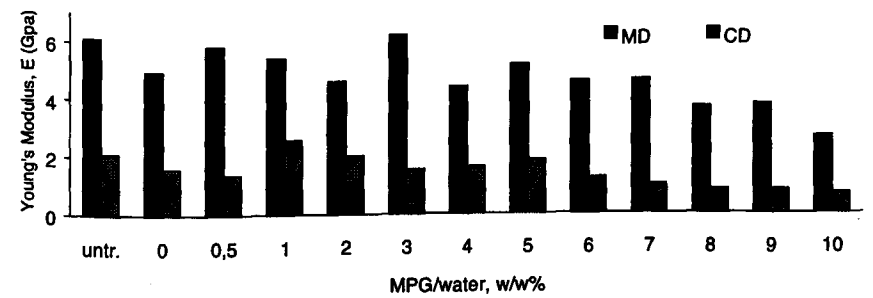
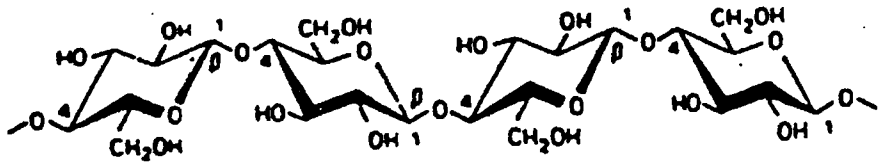


Fig. 11: Changes in elasticity of photocopy paper wettet in MPG/water

The crystalline structure of cellulose is well characterized. The unit cell of native cellulose (cellulose I) consists in four D-glucose residues. In the chain direction, the repeating unit is a cellobiose residue (1,03 nm) and every glucose residue is accordingly displaced 180° with respect to its neighbours, giving cellulose a 2-fold screw axis. It is largely accepted that all chains in native cellulose microfibrils are parallel, that is, are oriented in the same direction. There are two intramolecular hydrogen bonds within each cellulose chain, namely from O(6) in one glucose residue to O(2)H in the adjacent glucose and also from O(3)H to the ring oxygen (O5). The chains form a layer in the a-c crystallographic plane, where they are held together by hydrogen bonds from O(3) in one chain to O(6)H in the other chain. There are no hydrogen bonds in cellulose I between these layers, only weak Van der Waals forces[34] in the direction of the b-axis.

Conclusion

In our case, the paper sheets immersed in aqueous alkoxypolyethyleneglycol solutions are affected by the following phenomena:



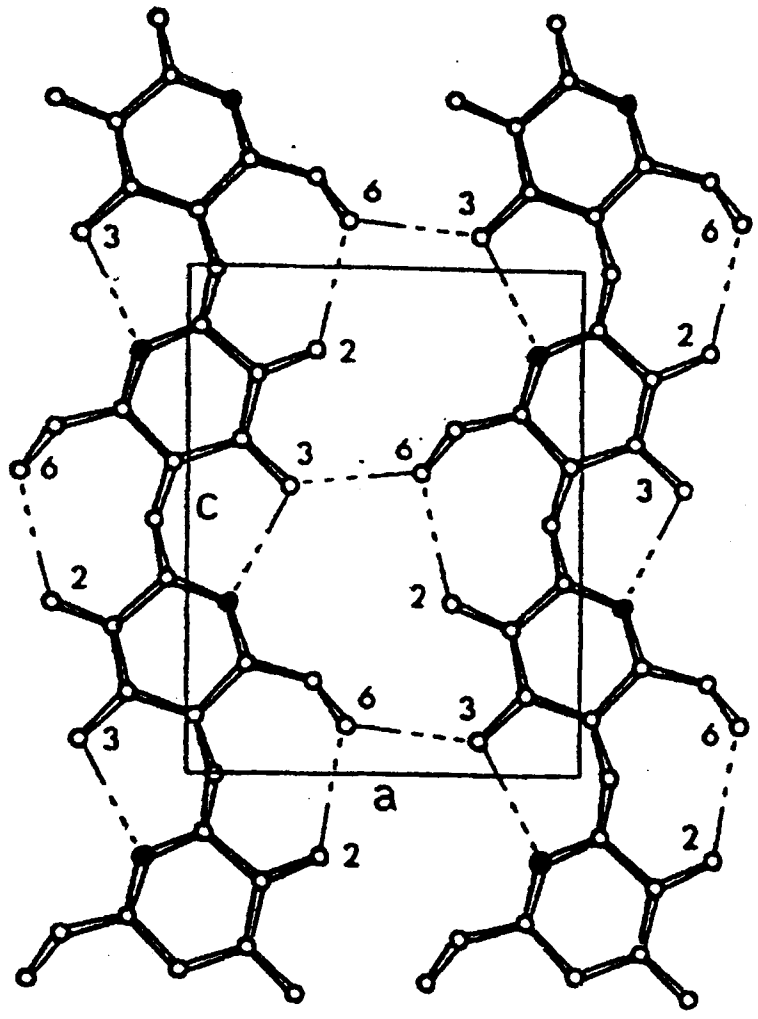
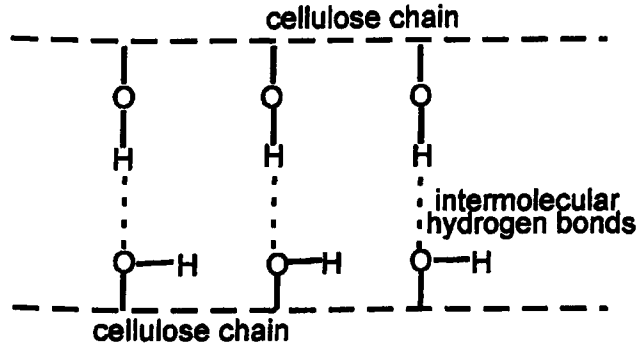


Fig. 12: Structure of cellulose, showing the intermolecular and intramolecular hydrogen bond



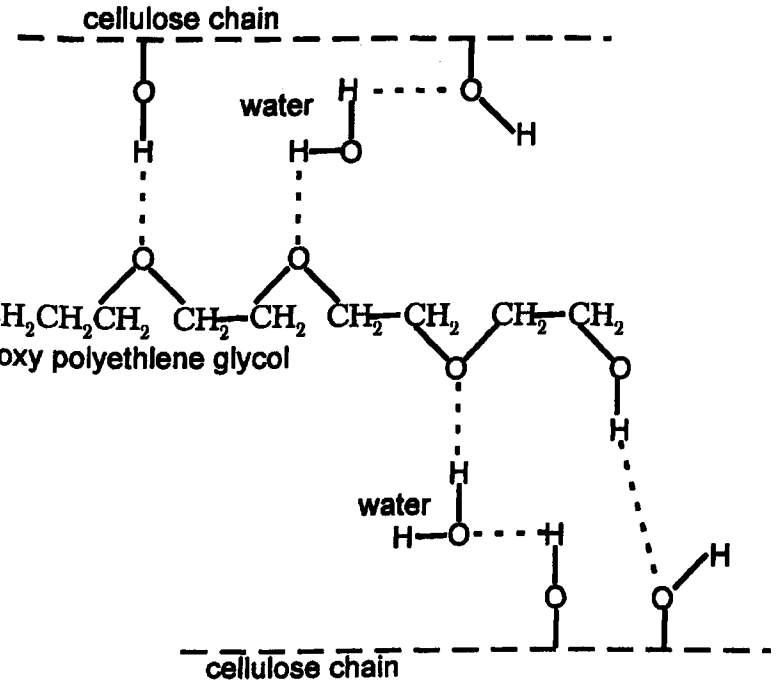


Fig. 13: Scheme of hypothetical interaction between cellulose, alkoxy polyethylene gylcol and water, before (upper part) and after treatment (beyond): Formation of hydrogen bonds between cellulose and water and BTG molecules and failure of the cellulose intermolecular network

- Water and alkoxypolyglycol molecules penetrate within the cellulose fibers network filling the pores and empty volumes between the fibrils.
- Water and alkoxypolyglycol molecules interact with cellulose via formation of hydrogen bonds. Some interfibrillar or intrafibrillar hydrogen bonds in cellulose chains can be broken and substituted by hydrogen bonds with water or polyglycol molecules.
- When water evaporates and paper dries up to equilibrium with atmospheric humidity, most of water previously adsorbed disappears, and paper sheets recover partially their initial dimensions. Some curling is observed, due to aniso-ropy of paper.
- Alkoxyglycols are non-volatile liquids, so they remain permanently within the paper after drying, forming strong hydrogen bonds with cellulose. They are not easily removed by subsequent washings.
- Paper treated with aqueous solutions of alkoxypolyglycols shows an increase in weight (grammage) and thickness, as a consequence of absorption and swelling. This is not only caused by alkoxypolyglycol molecules, but also by water vapour, as hygroscopicity of paper becomes increased.
- The loss of mechanical strength has been extensively demonstrated by using most of the different tensile and bending parameters currently recommended. The trend lines have always negative slopes in every case, so that a permanent modification of the paper structure is caused.
- The longer the polyglycol molecule is, the greater is the softnening effect on the paper.

FINAL COMMENT

Results of treatment with aqueous solutions cannot be compared, in principle, with results of deacidification treatments performed with non-polar solvent solutions containing magnesium derivatives of the same kind of polyglycols, because mechanism of sorption of organic solutions by paper is completeley different than sorption of water. Nevertheless, and assuming that after a slow atmospheric hydrolysis, mass-deacidified paper becomes impregnated with free poyglycols and covered by a deposit of magnesium carbonate, the negative effects of polyglycols on the properties of paper would be more apparent after a long period of time in contact with moist air, or in case of accidental wetting, for example.

ACKNOWLEDGEMENTS

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APPENDIX: ELASTICITY OF PAPER – CALCULATION OF YOUNG'S MODULUS[15]

Young's modulus (E_0) of a bone dry paper at a standard temperature of 25° C, water content of paper 0%:

$$E_0 = N^{1/3} \langle kR \rangle$$

where:

- N: Number of effective intermolecular hydrogen bonds per unit volume (m^3) in taking up strain under uniaxial stress conditions.
- <kR>: Force constant for stretching the bond. In paper, <kR> 18,42 N/m, corresponding to an H-bond energy of 4,75 kcal/mol.

$$N = (6 * NA * \rho * \beta) / (3 * 0{,}324)$$

where:

- 6: Number of hydrogen bonds per anhydrocellobiose unit
- N_A: Avogadro's number
- α: 1540 kg/m3: apparent density
- β: Fraction (2/3) of the total number of hydrogen bonds used in intermolecular bond.
- 3: Fraction of hydrogen bonds oriented along the three orthogonal axes: 1/3
- 0,324: Molecular weight of the anhidrocellobiose unit in kg/mol

$$N = 3{,}8 * 1027 \text{ hydrogen bonds; } E_0 = 28{,}79 \text{ GPa}$$

Young's modulus (E) of a well-bonded isotropic paper sheet in a room at 50% RH, that is, with a moisture content of 6%. By applying two equations for temperature and moisture corrections, it is obtained the value of E = 25 GPa, that is, 86,8% E_0.

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Application to photocopy paper used in this study

From the grammage (80 g/m^2) and thickness (0,109 mm) measured at 50% RH, an apparent density of 733,8 kg/m3 is obtained. Thus, N = 1,8 * 1027 effective hydrogen bonds, and finally:

$$E_{pap50} = 19{,}5 \text{ GPa} \quad \text{that is,}$$
$$78{,}1\% \; E_{cell50}$$

This result corresponds to an ideal isotropic paper, with the same density of the real paper, and neglecting the contribution of other components of paper, like lignin, sizing agents, fillers.

Youngs modulus determined from tensile tests in the elastic regime

Experimental Young's modulus is obtained from the values of elastic limit and elongation at the elastic limit given from the strain-stress graph for a single specimen test. Greatest values obtained are 12,5 GPa, in machine direction, and 2,6 GPa, in cross direction, both corresponding to untreated paper. Water reduces elasticity, and polyglycol increases this reduction.

Similar tests conducted on a calendered printing paper, grammage 60 g/m^2 and apparent density1240 kg/m^3, have given the following results: E (theoretical, isotropic): 23,2 GPa. Maximum values found: 16 GPa (MD), 4,3 GPa(CD).

SUMMARIES

The effect of aqueous solutions of alkoxypolyethyleneglycols on the properties of paper

From the results obtained in some mass deacidification tests using compounds based on magnesium alkoxypolyethyleneglycolates, we suspected that the glycols left within the paper after the treatment could diminish the paper strength. The atmospheric hydrolysis and carbonatation of the magnesium reagents applied on the paper produced magnesium carbonate and long-chain glycols. To confirm this suspicion, we treated separately several modern paper samples with aqueous solutions of glycols and magnesium bicarbonate, and found that the values of tensile strength and folding endurance were reduced as the solute concentration increased. This effect is much more noticeable in the case of glycols. An attempt is made to explain theoretically these results by means of the chemical interaction between long-chain alkoxypolyethylenglycols and cellulose network via hydrogen bonding.

L'effet de solutions aqueuses d'alkoxyde polyéthylène glycol sur le papier

D'après les résultats observés sur les objets qui ont été soumis à un test de désacidification de masse au moyen de produits à base d'alkoxyde polyéthylène glycol de magnésium, nous supposions que les glycols restés dans le papier après le traitement pourraient réduire la solidité du papier. L'hydrolyse et la carbonatation des réactifs de magnésium appliquées au papier ont produit du carbonate de magnésium et des glycols à longue chaîne moléculaire. Afin de vérifier cette hypothèse nous avons traité séparément différentes sortes modernes de papier avec des solutions aqueuses de glycols et de bicarbonate de magnésium, et nous avons observé que les valeurs de résistance à la traction et au pliage diminuaient en fonction de l'augmentation de la concentration de la solution de polyglycol. Cet effet est d'autant plus prononcé avec un glycol de poids moléculaire plus important. On tente d'expliquer ce phénomène par des réflexions théoriques sur l'interaction chimique entre les alkoxydes polyéthylènes glycols à longue chaîne moléculaire et la molécule réticulée de la cellulose via un pont d'hydrogène.

Die Wirkung wäßriger Lösungen von Alkoxypolyäthylenglykolen auf Papier

Aus Beobachtungen an Objekten, die einer Massenneutralisierung im Veruch auf der Basis von Alkoxypolyäthylenglykolaten unterworfen waren, ergab sich die Vermutung, daß die Glykole, die nach der Behandlung im Papier zurückbleiben, die Festigkeit des Papiers vermindern könnten. Die Hydrolyse und Aufnahme von CO_2 des magnesiumhaltigen Stoffes im Papier führt dort zu Magnesiumcarbonat und zu langkettigen Glykolen. Um diese Vermutung zu bestätigen, behandelten wir verschiedene moderne Papiere mit wäßrigen Lösungen von Glykolen und Magnesiumbicarbonat, und wir fanden, daß die Werte für Bruchkraft und Falzfestigkeit mit steigender Konzentration des Polyglykols sanken. Dieser Effekt ist weitaus deutlicher bei dem Glykol mit höherem Molekulargewicht. Es wird versucht, dieses Phänomen durch theoretische Überlegungen zur Reaktion über Wasserstoffbrücken zwischen dem langkettigen Molekül des Alkoxypolyethylenglykol und dem netzartigen Cellulosemolekül zu erklären.

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The Positive Effects of Air Purification in the Dutch State Archives

Part 1: Experimental Set up and Air Quality

by MARGA DE FEBER, JOHN HAVERMANS & ERIC CORNELISSEN

INTRODUCTION

Many national and international research programmes study the "acidification of cultural heritage"[1–5].

Acidification of paper takes place as a consequence of internal and external factors and this process can only be ceased in one way: deacidification. Since deacidification usually is a laborious and expensive business, research is carried out to develop suitable mass deacidification methods. At present only a few methods are fulfilling the requirements as given by the Dutch State Archives: the DEZ gaseous deacidification method[6], and the modified Bookkeeper process. The first one however, is now discontinued. Nevertheless, it will take a lot of time to deacidify the 80-km extensively acidic paper collection of the Dutch State Archives. Therefore measures must be taken to prevent further acidification of archival materials. One way to achieve this is for instance air purification[3]. Previous research has shown that air pollutants like SO_2 and NO_x accelerate the ageing of paper, and that reactivity is increased with increasing relative humidity[2,4,7,8]. Air purification therefore possibly decreases the influence of external factors on the acidification and as such reduces the deterioration of paper by air pollutants. It must be emphasized however that air purification cannot stop the process of acidification itself, since internal factors arise from the paper itself[1,9]. Concerning the internal factors, several authors stated that acidification is generally less occurring in alkaline papers, and moreover they stated that it is improper to draw conclusions based on mechanical properties only[10].

In 1994, the Dutch State Archives put into use a new air conditioning and purification system[11–12]. At the same time TNO was commissioned to investigate the effects of this newly installed system. The project described here aims to control the functioning of the new system, and to investigate the ageing behaviour of papers stored under the "clean" or the "dirty" environmental conditions. Based

Table 1: Archival storage conditions according to R. Vosteen[13].

Temperature	Relative humidity	Ventilation rate	Circulation rate	Air velocity
18 °C ± 2 °C	50% ± 5%	0.2 h^{-1}	2.0 h^{-1}	Minimum 0.01 m/s

on former research and the recommended guideline for air quality in archives[13], archival storage conditions were set as shown in Table 1.

This paper is the first out of a series of three describing the effects of air purification on the ageing of paper in the Dutch State Archives. The experimental set up is described here, as well as the first results obtained from the air quality measurements. Parts two and three will respectively describe the results of pollutant and paper measurements. Both are foreseen to be published this year.

AIM OF THE PROJECT

The aim of the project referred to as the "reference depot" is to determine the long-term effect of cleaned storage rooms on the ageing behaviour (durability) of paper. To reach this aim the extent of paper decay in relation to its storage conditions will be evaluated for at least ten years.

EXPERIMENTAL SET UP

General

The research takes place in the building of the General State Archives, located in the urban area of The Hague (The Netherlands). This makes the experiments unique since they are taken in a realistic instead of a laboratory situation. For a period of ten years minimum, test materials are stored in two archival storage rooms: one with and one without air purification. Periodically, samples are taken to evaluate the changes in the stored papers. The changes are related to other measures that take place in the storage rooms, e.g. the amount of air pollutants, ventilation rate and air velocity.

Storage rooms

Both test rooms are situated in the building of the General State Archives in The Hague. One room is connected to the new air cleaning and conditioning system

and called the *test depot*. The second room has no air purification system and is referred to as the *reference depot*. The reference depot was especially prepared for this project since at the start all rooms in the building already had some form of air purification.

- Test depot
  This room is not especially enclosed but forms part of an overall storage room that is provided with the air purification equipment. The total volume of the storage room is circa 2500 m^3. The volume of the test depot is circa 165 m^3.
- Reference depot
  This is an enclosed room that is only accessible for authorised people. The reference depot is in direct contact with the outdoor air and recirculation takes place without purification. The volume of the room is circa 143 m^3.

Materials

For this project both old naturally aged papers and new defined reference materials are used. These will be referred to as "old" and "new" materials. The new materials were especially made for the EC STEP CT90-0100 project[7], and therefore production manner, composition and ageing behaviour are well defined. The old materials originate from the Dutch State Archives. The ageing characteristics of the papers are measured yearly using the samples coming from the stored materials. Sample preparation is described below.

Sample preparation

The sample preparation of new materials is illustrated in Fig. 1. Since these materials were specially produced, they are of homogeneous composition. The following paper grades are used:

- bleached-sulphite softwood cellulose
- groundwood containing paper
- cotton linters cellulose.

Piles of sheets are cut to A4-format and stored in two different ways:

- unbound paper in acid free wrapping paper and boxes and
- storage as bound volumes

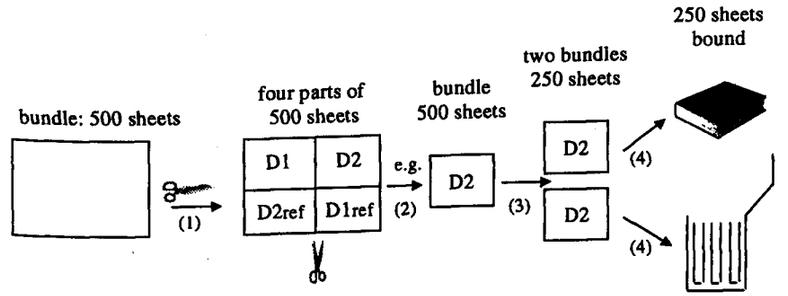

Fig. 1: Sample preparation of new paper materials

The archive boxes originate from the Dutch State Archives. In total 60 books are available of all material types. Of these books, 15 copies are kept in the test and reference depots. The other 30 copies are kept as reference materials in a climate room at TNO.

The sample preparation of old materials differs from that of the new materials. For this project, 18 volumes of various archival material (dating from 1872 to 1971) were made available by the Dutch State Archives. There were some complicating factors during sample preparation of these materials. Besides the heterogeneous quality of the papers, also the orientation during storage in the past has to be taken into account. The latter is very important since the top side of a volume has been in more direct contact with the surrounding air than the bottom side. The sample preparation of old materials and distribution among both depots was done using a statistically developed experimental design, developed in co-operation with the department of Applied Statistics of the TNO Institute of Applied Physics[14]. All quarters of a volume are bound again after the cutting procedure. Materials of each sample are stored in both test and reference depot (Fig. 2).

MEASUREMENTS

The measurements in both depots are divided into measurement of the environmental conditions on one, and the material quality on the other hand. These parameters are measured in different ways as described below.

Fig. 2: Storage of the samples. On the left the old, on the right the new materials, bound and packed in boxes.

Environmental conditions

On line air pollutants

For both depots concentrations of different air pollutants are measured continuously, i.e. sulphur dioxide (SO_2), nitrogen oxide (NO), nitrogen dioxide (NO_2), the total of the nitrogen oxides (NO_x) and ozone (O_3). For this purpose three analysers are placed in both storage rooms (produced by Advanced Pollution Instrumentation Inc., API). The data are compiled and stored using a computer provided with data acquisition software. The data are converted and visualized using a programme enabling to compare the data (e.g. average, minimum and maximum) each week, month or year.

Air corrosiveness

The air corrosiveness (aggressivity) is measured using On Guard monitoring systems. This measurement is based on the corrosion of copper and silver by oxidizing components present in the air (e.g. SO_2, O_3). As a consequence of the reaction metal oxides are damped on the crystals which are vibrating in the On Guard system. The more corrosion will take place, the less the crystals will vibrate. The decrease in vibration (Hz) is calculated in Ångstrom. Besides the corrosiveness, temperature and relative humidity are also continuously monitored by the On Guard system. Furthermore, temperature and relative humidity are measured by the air conditioning system itself.

Air quality

In both storage rooms ventilation and recirculation conditions are measured yearly by means of measuring the air supply and discharge (m^3/s), air ventilation (1/h), air recirculation (1/h) and air velocity (m/s) at various locations.

Material quality

To determine the degree of ageing of the stored materials, samples are taken yearly from the test and reference depot. For this purpose a sampling procedure have been developed. Selected mechanical, physical and chemical paper characteristics are subsequently determined (e.g. pH-value of the cold water extract of the paper according to NEN 2151, folding endurance according to ISO 5626, and yellowing of the paper according to DIN 6167).

RESULTS AND DISCUSSION

As stated previously this paper describes the interim results concerning the first four years. This paper will focus on air quality only. The results on pollutant concentrations and paper quality will be published separately.

Air Quality

At the beginning of the project in 1994, a reference measurement was done to record the situation of the indoor climate in both test and reference depots. Every year, this measurement is repeated. The results up to now are summarized below. In the calculations, the following definitions were used:

Air circulation rate

This is the number of times that the air in the archival storage room is circulated per hour. The circulation rate is based on the sum of all supplied (or discharged) air, which means open air as well as recirculated air. A circulation rate of at least 2.0 h^{-1} is recommended in the guideline[13].

Table 2: Air quality measurements test depot

Parameter	Units	Guideline	1994	1995	1996	1997
Air supply	m^3/s	1.39*	0.404	0.396	0.385	0.408
Air discharge	m^3/s	**	0.234	0.200	0.318	0.329
Circulation rate	h^{-1}	2.0	0.58	0.57	0.55	0.59
Ventilation rate***	h^{-1}	0.2	0.14	0.21	0.17	0.16
Air velocity	M/s	>0.01	0.09	0.08	0.08	0.09

* Knowing the volume of the test depot, the required air supply can be calculated from the advised circulation rate.

** Since there is an overpressure in the test depot, the circulation rate should be based on the air *supply*. Therefore a guideline for the air discharge is not of relevance here.

*** Calculated from the summoned open air flow in North and South depots (the test depot forms part of the South depot), assuming that ventilation rate is of the same magnitude in both depots.

Air ventilation rate

This is the number of times that the air in the archival storage room is completely replaced by open air per hour. The ventilation rate is based on supplied open air only. A ventilation rate of at least 0.2 h^{-1} is advised in the guideline[13].

The development of the circulation and ventilation rate in the test depot is graphically shown in Fig. 3 (cf. also Table 2). From this figure it is clear that the circulation rate has been much too low (around one fourth of the advised value) during the last four years. In 1998, measures have been taken to adjust the circulation in the test depot.

Also the ventilation rate has been too low (average 85% of the guideline) with the exception of the year 1995. Therefore the intake of open air is also a point of interest.

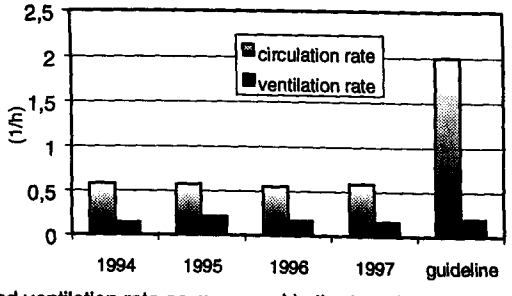

Fig. 3: Circulation and ventilation rate as measured in the test depot. At the right the value according to Vosteen's guideline is given.

Table 3: Air quality measurements at reference depot.

Parameter	Units	Guideline	1994	1995	1996	1997
Air supply	m^3/s	... *	0.020	0.024	0.013	0.017
Air discharge	m^3/s	0.079**	0.027	0.047	0.055	0.059
Circulation rate	h^{-1}	2.0	0.7	1.2	1.4	1.5
Ventilation rate***	h^{-1}	0.2				
Air velocity	m/s	>0.01	0.08	0.10	0.08	0.09

* Since there is a low pressure in the reference depot, the circulation rate should be based on the air *discharge*. Therefore a guideline for the air supply is not of relevance here.

** Knowing the volume of the reference depot, the required air discharge can be calculated from the advised circulation rate.

*** Ventilation rate in the reference depot is unknown, since the magnitude of the open air flow was not measured separately up to now.

The development of the circulation rate in the reference depot is graphically a shown in Fig. 4 (cf. also Table 3). From this figure it can be seen that the circulation rate has increased during the years, but that the optimum value according to the guideline is still not realized.

The most important changes in the air quality conditions that were observed are summarized as follows (reference year 1994):

- The air supply in the test depot has increased slightly in the last year, after a decrease in the former two years.
- The air discharge in the test depot has increased by 40% when compared with the situation in 1994.
- The air supply in the reference depot has decreased by 15% when comparing the most recent situation with the one in 1994.

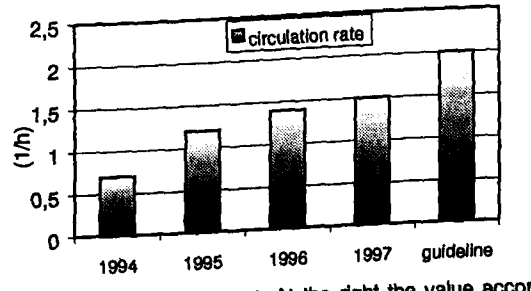

Fig. 4: Circulation rate in the reference depot. At the right the value according to Vosteen's guideline is given.

- The air discharge in both test and reference depots has increased significantly when compared with the situation of 1994, respectively by 40 and 120%.
- The circulation rate in the test depot has been much too low during the last four years.
- The ventilation rate in the test depot has been just too low in the test period so far, with the exception of the year 1995.
- The circulation rate in the reference depot has increased during the years, but the optimum value according to the guideline is still not realized.
- At the moment it is not possible to pass sentence on the ventilation fold in the reference depot, since the open-air flow was not measured separately.
- The average air velocity varies 10–20% over the years but according to various (local) measurements; the air velocity meets the minimum requirement of 0.01 m/s on every position in both depots.

In 1998, measures have been taken to adjust the circulation in the test depot. It is expected that these will improve the air quality situation in this archival storage room. From this year on, also the ventilation rate in the reference depot will be determined.

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The Dutch State Archives are highly acknowledged for funding this research, especially Mr. Ted Steemers for his counterpart in managing this project. By means of this paper, the authors would like to acknowledge Mr. Ronald van Deventer, who was involved in setting up this project.

SUMMARIES

The positive effects of air purification in the Dutch State Archives. Part 1: Experimental set up and air quality

One of the measures for preventive conservation in archives, libraries and museums is air purification. Based also on the results of the European Research Programme in the STEP framework *The Effects of Air Pollutants on the Accelerated Ageing of Paper* the Dutch State Archives in The Hague renewed their indoor air quality system in 1994. In order to prove the positive effects of the new air quality and purification system, a 10-year pilot research project was started. Two archival storage rooms are used; one with and one without air purification. In both rooms test materials are stored. The level of air pollutants (SO_2, NO, and O_3), temperature and relative humidity are measured continuously while the air quality (ventilation and recirculation rate) and the paper quality (in terms of chemical, mechanical and physical properties) are measured yearly.

In a series of three papers the interim results of the project are discussed. This is the first paper discussing air quality. It was concluded that during the last four years the circulation rate in the reference depot (i.e. without air purification) has been increased. It is about to come closer to the value stated in archival guidelines (i.e. 2 1/h). Furthermore it has been concluded that the circulation rate in the test depot (i.e. with purification) is still far beneath the given value. Therefore the ventilation shafts have been replaced.

Les effets positifs de la purification de l'air dans les Archives nationales hollandaises

La purification de l'air environnant est une des mesures préventives pour la conservation dans les archives, les bibliothèques et les musées. Sur la base des résultats du programme européen de recherche réalisé dans le cadre du STEP concernant *Les effets des gaz environnants sur le vieillissement accéléré du papier* les Archives nationales hollandaises à La Haye ont remplacé en 1994 leur système d'aération. Un projet pilote de recherche d'une durée de 10 ans a été mis en place dans le but de prouver les effets positifs de la nouvelle qualité de l'air et du système de purification. Deux salles où sont déposées des archives font l'objet de l'étude: l'une étant raccordée au système de purification de l'air, l'autre non. Les quantités de gaz environnants (SO_2, NO_2, et O_3), la température et l'humidité relative sont mesurées continuellement alors que la qualité de l'air (ventilation et taux de recirculation) et la qualité du papier (en termes de propriétés chimiques, mécaniques et physiques) sont mesurées une fois par an. Dans le premier des trois rapports au total sur le projet on discute des résultats provisoires obtenus. Il décrit la qualité de l'air. D'après les résultats on arrive aux conclusions suivantes : au cours des quatre dernières années le taux de circulation s'est amélioré dans le dépôt de référence (c-à-d. dans la salle non raccordée au système de purification de l'air). Elle se rapproche des valeurs recommandées par les directives dans ce domaine (2 1/h).

Par ailleurs on a observé que le taux de circulation de l'air dans le dépôt témoin (c-à-d avec purification de l'air) se situe toujours bien au-dessous de la valeur donnée. C'est pour cette raison que les conduits d'arrivée d'air ont été remplacés.

Die positive Wirkung von gereinigter Luft im holländischen Staatsarchiv. Teil 1: Installation für das Experiment und Luftqualität

Eine der Möglichkeiten der vorbeugenden Konservierung in Archiven, Bibliotheken und Museen ist die Reinigung der Umluft. Auf der Grundlage der Ergebnisse des im Rahmen von STEP durchgeführten europäischen Forschungsprogramms über *Die Wirkungen von Umweltgasen auf die beschleunigte Alterung von Papier* erneuerte das holländische Staatsarchiv in Den Haag im Jahre 1994 sein Belüftungssystem. Um die positiven Wirkungen des neuen Systems, das auch ein Reinigen der Luft beinhaltet, zu verifizieren, wurde ein auf zehn Jahre befristetes Projekt aufgelegt: Zwei Räume mit Archivgut werden beobachtet, der eine mit und der andere ohne Anschluß an das Belüftungssystem. Die Mengen der Umweltgase (SO_2, NO, und O_3), die Temperatur und die relative Luftfeuchtigkeit werden kontinuierlich, die Kennzahlen des Luftaustausches (Ventilation, Umwälzung) sowie die Papierqualität (chemische, mechanische und physikalische Eigenschaften) werden jährlich gemessen.

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In diesem ersten Bericht von insgesamt drei werden vorläufige Meßdaten diskutiert. Er beschreibt die Luftqualität. Aus den Ergebnissen wird geschlossen, daß sich im nicht belüfteten Raum die Luftumwälzung während der letzten vier Jahre verbessert hat. Sie nähert sich dem in einschlägigen Richtlinien empfohlenen Wert (2 1/h) an. Weiterhin wird geschlossen, daß die Luftumwälzung im belüfteten Raum noch weit unterhalb des eingestellten Wertes liegt. Deshalb wurden die Luftzuführungsschächte erneuert.

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