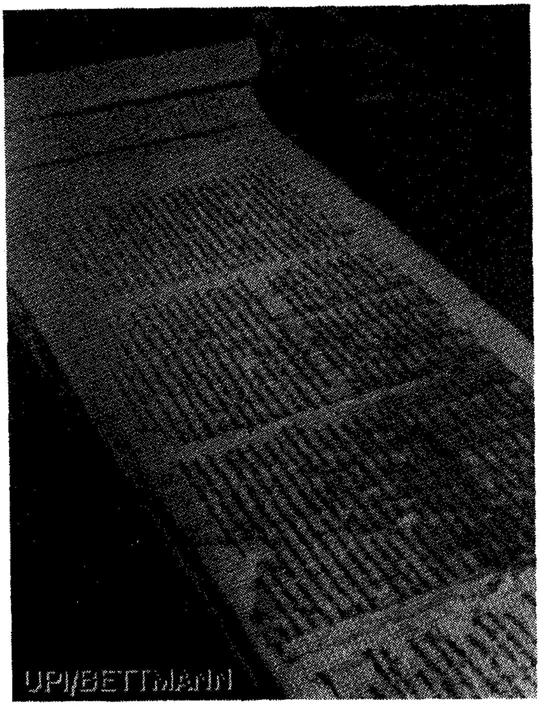
Propositions **Stellingen**

ENVIRONMENTAL INFLUENCES ON THE DETERIORATION OF PAPER



John Havermans

18 September 1995

-1-

- The more one goes back in history, the more durable the information carriers are.
- Hoe verder wordt teruggegaan in de geschiedenis des te duurzamer de mediadragers zijn.

Encarta 1994 Edition, Multimedia Encyclopedia. Microsoft Corporation, 1993; Rogerson, J., 1985. The New Atlas of the Bible, Equinox (Oxford), 16-22.

-2-

- Current testing methods for the accelerated ageing of paper are less applicable for modern alkaline writing papers and ancient deacidified papers.
- De huidige testmethoden voor de versnelde veroudering van papier zijn minder effectief op moderne alkalische en ontzuurde papieren.

This thesis, 5: 134-140, 6: 165-166, TAPPI T 453 pm, 1985, 1-3 ; ISO 5630/1, 1982, 232-233; ISO DIS 9706, 1992, 1-2; Havermans, J.B.G.A. and R.P. van Deventer, 1995. Mass deacidification, the DEZ-process and the Battelle-process compared. Proceedings of the satellite meeting on Library Preservation and Conservation in the 90s. Budapest, August 1995, 18-20.

-3-

- To establish the leaching characteristics of impregnated timber by creosote tar oil, only 4 PAH compounds have to be analysed in time, *i.e.* phenanthrene, anthracene, fluoranthene, and pyrene.
- Voor het vaststellen van de uitloogkarakteristieken van creosoot uit verduurzaamd (gecreosoteerd) hout behoeven slechts 4 PAK verbindingen in de tijd te worden geanalyseerd, deze zijn fenantreen, antraceen, fluorantheen en pyreen.

Boonstra, M.J., et al., 1991. Evaluatie van onderzoek naar de uitloogkarakteristieken van verduurzaamd hout, TNO-Bouw, Centrum voor Houttechnologie, Rapport No. B-91-0082, Projectnummer 2034012, Bijlage 2.

-4-

- After the conservation of paper by means of deacidification, it will almost be impossible to date the paper on the basis of the inorganic fillers.
- Na het conserveren van papier door ontzuring, wordt het vrijwel onmogelijk om papier te dateren op grond van zijn anorganische samenstelling.

Browning, B.L., 1977. Analysis of Paper 2nd ed., Marcel Dekker, New York, 334-337; This thesis, 6: 158.

- 5 -

- The acetylation of timber will lead to a decrease of its biodeterioration. It should be realised, however, that concurrently the chemical deterioration might increase.
- Hoewel het acetyleren van hout leidt tot een verlaging van de biodegradatie, moet er echter rekening worden gehouden met een toename van de chemische degradatie.

Rowell, R.M., 1983. Chemical modification of wood. Forest Products Abstracts, 6, 12.

- 6 -

- In the search for an effective method to stop paper deterioration by ink-corrosion, more attention should be paid to the effects of two reactions occurring simultaneously during the ink-decay process, *i.e.* the oxidation of Fe(II)ions and the hydrolysis of cellulose.
- Bij het zoeken naar een effectieve methode om inktvraat tegen te gaan, wordt te weinig aandacht besteed aan de combinatie van reacties die gelijktijdig optreden, te weten de oxydatie van ijzer(II)ionen èn de hydrolyse van cellulose.

Sistach, M.C. and I. Espadaler, 1993. Organic and inorganic compounds of iron-gall inks. ICOM Committee for Conservation, Proceedings of the 10th triennial meeting, Washington D.C., 485-489.; Berkhout, S.A. and J.B.G.A. Havermans, 1994. Simulatie en identificatie van inktvraat in papier, veroorzaakt door ijzergalinkten. De Restaurator 24: 5-12; Neevel J.G., 1995. Phytate: a potential conservation agent for the treatment of ink corrosion caused by iron-gall inks. Proceedings of the interim meeting of the ICOM Committee for Conservation, Amsterdam, 1-5.

- 7 -

- Proposition (7) of Neevel has to be generalised. The mechanical damage caused by the public use of documents or books, is the greatest threat to our paper-based cultural heritage.
- Stelling (7) van Neevel dient te worden veralgemeniseerd. De mechanische schade die ontstaat bij het raadplegen en/of kopiëren van documenten of boeken, is de grootste bedreiging die ons papieren cultuurgoed kent.

Neevel, J.G., 1992. The biacetyl-azo dye systems. A model system to investigate oxidative dye fading, Thesis proposition No. 7, Delft University of Technology.

-8-

- More attention should be paid to the philosophy of science according to K.R. Popper "Success for a scientific theory is the passing of a test - the survival of an attempt to falsify the theory".
- Werken volgens de wetenschapsopvatting van K.R. Popper, "Een succesvolle wetenschappelijke theorie wordt gekenmerkt, doordat ze bestand is tegen pogingen om ze te falsificeren", verdient meer aandacht.

Gadellaa, J., 1985. Een filosofische en sociologische kijk op de wetenschap, Reader Chemie & Samenleving, Universiteit van Utrecht, 7; Collingridge, D., 1975, The Testing of Scientific Theories. An Introduction to the Philosophy of Science. Reader University of Aston, Technology Policy Unit, 4-6.

-9-

- The legislation of the Dutch "Warenwet", coded C1-35b, takes no account of the fact that wood based boards other than particle-board, can emit formaldehyde as well.
- Het uitvoeringsvoorschrift van de Warenwet (C1-35b), houdt geen rekening met het feit, dat ook plaatmaterialen anders dan spaanplaat, het zogenaamde spaanplaatgas (formaldehyde) kunnen afgeven.

Besluit van 26 augustus 1986 (Staatsblad 517), houdende regelen met betrekking tot spaanplaat, Spaanplaatbesluit Warenwet; Havermans J.B.G.A., 1988. Performance of the formaldehyde emission method CEN CR-213 (1984). In: Zur Messung von Formaldehyd-Methoden. Erkenntnisse und Erfahrungen, WKI-Bericht Nr. 19. Ed. R. Marutzky, Fraunhofer-Institut für Holzforschung, Wilhelm-Klauditz-Institut, 282.

-10-

- There is a serious risk for fraud if all know-how of the information on optical security documents will be made available to the public.
- Het verspreiden van de inhoudelijke kennis over optische documentbeveiliging kan leiden tot een verhoging van fraude van o.a. waardedocumenten.

Moser, J.F., 1993. Protection by optically variable graphics (kinegram). In: Optical Document Security. Ed. R.L. van Renesse, Artech House, Boston, 169-172.

-11-

- The role of conifers on the SO_2 and O_3 reactions in our atmosphere, is often disregarded.
- De invloed van naaldhoutbomen op de SO_2 en O_3 huishouding in onze atmosfeer, wordt veelal veronachtzaamd.

Kotiaz, D., et al., 1990. Reaction of monoterpene hydrocarbons with O_3, SO_2 and NO_2 formation of acidic compounds. In: Physico-chemical behaviour of atmospheric pollutants. Ed. G. Restelli and G. Angeletti, Kluwer Academic Publishers, Dordrecht, 394-397.

- 12 -

- Although the manufacturer of Kurzweil synthesisers, Young Chang, states that the sound synthesis technique “Variable Architecture Synthesis Technology” is one of the most modern and advanced synthesis techniques, it has to be considered that the principles of this technique were already used in the MOOG modular synthesisers of 1964.
- Hoewel de fabrikant van de Kurzweil synthesizers, Young Chang, de in zijn produkten toegepaste geluidsynthese techniek, “Variable Architecture Synthesis Technology”, beschrijft als een van de meest moderne en geavanceerde synthese technieken, dateert dit principe reeds uit de tijd (1964) van de modulaire MOOG synthesizers.

Deutsch, H.A., 1976. Synthesis, an introduction to the history, theory & practice of electronic music. Alfred Publishing Co., New York, 31-35; Anonymous, 1992. Kurzweil K2000 Musician's Guide Version 2. Tech Cetera USA, Young Chang Akki Co., LTD, 1.1-1.3.

- 13 -

- The ageing of paper is characterised by two phenomena.
  1) The acidification of paper by air pollutants will lead to an *increase* in the crystallinity of cellulose, and results in a decrease in its equilibrium moisture content, and
  2) By contrast, thermal ageing of paper will lead to a *decrease* in the crystallinity of cellulose, but results also in a decrease in its equilibrium moisture content (hornification).
- De veroudering van papier wordt gekenmerkt door een tweetal fenomenen.
  1) De verzuring van papier door luchtverontreinigingen leidt tot een *toename* in de kristalliniteit van cellulose die gepaard gaat met een afname van het evenwichtsvochtgehalte, en
  2) De thermische veroudering van papier leidt daarintegen tot een *afname* van de kristalliniteit van cellulose, welke echter ook gepaard gaat met een afname van het evenwichtsvochtgehalte (verhoorning).

This thesis, 2: 69, 3: 90-91, 5: 131-132.

- 14 -

- Word processing programmes like WordPerfect and Microsoft-Word, are not durable.
- Tekstverwerkingsprogramma's, zoals WordPerfect en Microsoft-Word, zijn niet duurzaam.

Environmental Influences on the Deterioration of Paper

Environmental Influences on the Deterioration of Paper

Proefschrift

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus Prof. ir. K.F. Wakker
in het openbaar te verdedigen ten overstaan van een commissie,
door het College van Dekanen aangewezen,
op maandag 18 september 1995 te 13.30 uur
door

Johannes Bernardus Gerardus Anthonius HAVERMANS

scheikundig doctorandus

geboren te Schiedam op 15 juni 1956

Environmental Influences on the Deterioration of Paper

Dit proefschrift is goedgekeurd door de promotoren
Prof.dr.ir. H. van Bekkum
en
Prof.dr.ir. J. van Turnhout

Samenstelling promotiecommissie:

Rector Magnificus,	voorzitter
Prof.dr.ir. H. van Bekkum,	Technische Universiteit Delft, promotor
Prof.dr.ir. J. van Turnhout,	Technische Universiteit Delft, promotor
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Dedicated to my dear wife Gerarda,
my parents and
my grandmother, who died in 1993.

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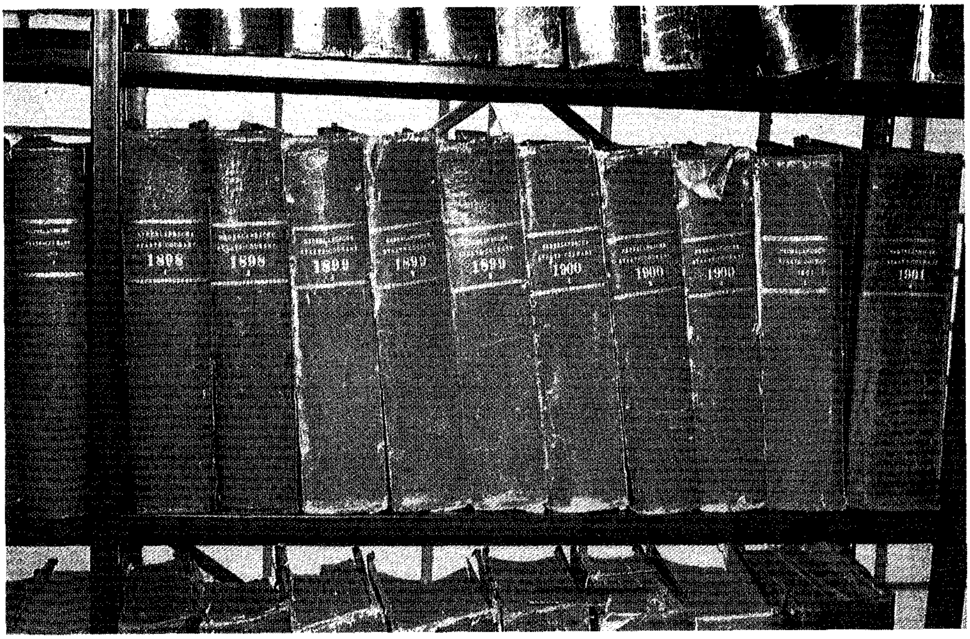
1

Introduction



1. INTRODUCTION

1.1 General

In this modern era of digitised information, it is sometimes forgotten that one of the oldest and most used media is paper. The long-term storage of paper records is not *per se* the main purpose of archives, libraries and museums, but rather to provide accessibility to the printed or written records. In order to serve this purpose, the paper materials must be "permanent", *i.e.* they must not deteriorate and become brittle or dark in colour.

The deterioration of books and archive materials due to acidification was first shown at the beginning of this century, although for almost two centuries the user of paper had raised the question "–What is the durability of paper and paper-made objects ?"

To answer this question, it is necessary to measure and interprete the changes in the material's performance. The performance of paper cannot be directly measured, but is generally related to the results of chemical and/or physical test methods. An understanding of the theoretical and actual material changes occurring, requires a knowledge of the overall composition of paper.

This chapter introduces the objectives and the background of this thesis, some parts of which were carried out within the framework of the European co-ordinated project "The synergistic effects of air pollutants on the accelerated ageing of cellulose-containing materials" (Havermans *et al.* 1994). This chapter also provides some (historical) background concerning the process of papermaking. Finally, some theoretical background to the problem of paper deterioration is given, together with a literature review of previous research carried out over recent years.

The *permanence* of paper is influenced by *internal* and *external* factors and by combinations thereof. The internal factors are introduced during the manufacture of the paper and include the type and quality of fibres, sizing materials, coatings *etc.*, and the presence of acidic compounds, metal ions, and other compounds in the paper sheet. The external factors are related to the conditions during storage or use, *e.g.* temperature, relative humidity, light and air pollutants. The biodeterioration or damage caused by insects may also be mentioned as an external factor. Although many investigations have been devoted to permanence, the factors influencing the stability and permanence of paper have not yet been fully established. Since many deterioration effects are attributed to the acidity of the paper, (mass)deacidification is often recommended. However, the contribution of the use of a deacidification process to the durability and especially the effects of air pollutants on deacidified materials are relatively unknown (Daniel *et al.* 1990), and need to be examined in more detail. The environmental factors causing deterioration of paper including *e.g.* temperature, oxygen and air pollutants have been studied in the work reported in this thesis.

1.2 Objectives

This doctoral study aimed at determining the effects of the environment (*e.g.* air pollutants and climate) on the stability of paper used and stored in archives and libraries. The study also included the effects of a mass-deacidification process on new acid paper materials.

1.3 A historical review

The origin of papermaking is somewhat obscure, but was almost certainly located in China. The first piece of paper, and thus also papermaking, may be credited to Ts'ai Lun about AD 105 (Turner 1991). Unfortunately, he did not leave enough paper to be investigated in this study.

Until the end of the 18th century, white papers could only be made of white rags, as the only method of bleaching was exposure to the sun. In one way, this was an advantage, as it avoided the deterioration of the paper by the bleaching agent. After the discovery of chlorine (1774) and hypochlorite (1789), these chemicals were soon used as bleaching agents, enabling coloured materials to be used for the production of white papers (Lanting *et al.* 1985; Schniewind *et al.* 1989).

The sizing of paper using rosin and alum $KAl(SO_4)_2$ was introduced by Illig (1805). Later the alum was replaced by $Al_2(SO_4)_3$, so-called papermaker's alum. Rosin size is a solution or dispersion obtained by treating rosin with a suitable alkali. Rosin is the residue obtained after distillation of the volatile matter from the gum of pine wood. When converted in the papermaking process, usually by the addition of alum, the size, an additive to make the fibre surface hydrophobic, precipitates and imparts water and ink resistance to paper (DePew, Jones 1992). This was in fact an unfortunate invention, because the hydrolysis of alum yields sulphuric acid, which can deteriorate paper. The first signals concerning the poor durability of these papers were heard already 150 years ago.

The increasing demand for paper exceeded the capacity of hand production and the supply of fibres previously used (Grant 1978).
In 1789, the Fourdrinier machine was invented by Robert in France and was soon extensively developed by the Fourdrinier brothers in England. With the enhanced production which this made possible, attention was directed towards other fibre sources than rags. One of the most promising and inexpensive alternatives was groundwood pulp. In 1844, Keller (Germany) developed a process for the manufacture of mechanical wood pulp. The wood pulp obtained was distinctly inferior, as the fibres were shorter, less pliable and still contaminated with the cementing lignin, but it was a cheap method and the potential supply was large. The disadvantage of the use of this groundwood pulp was that paper made with this material had a much shorter life span. At present, paper made between 1850 and 1880 has yellowed and embrittled to such an extent that books printed on this paper can no longer be used (Schniewind *et al.* 1989).

In 1851, willow wood was pulped by Burgess and Watt. Their process was improved in 1889 by Dahl. The wood was heated in a soda solution in order to dissolve the lignin in the wood and to release the cellulose fibre, and this resulted in a material with a pronounced colour. In 1867, Tilghman introduced an important development in wood pulping, the acid sulphite pulping. Here the fibre is produced by an acid chemical process in which the cooking liquor contains an excess of SO_2. This process came into operation in 1874. The sulphate or Kraft pulping process was developed a little later (1879), but was not taken into general use for printing and writing papers until the last few decades.

However, the use of wood fibres with cellulose having a lower molecular weight than that in cotton fibres combined with the pulping and bleaching processes meant that paper manufactured after 1850 was less durable than paper produced before 1850 (Lanting *et al.* 1985; Schniewind *et al.* 1989; Fellers *et al.* 1989).

1.4 What is paper?

Paper is a fairly random network consisting mostly of cellulose fibres (see also Figure 1.1). Although the fibre source has changed from cotton or linen rags to wood, its nature is still vegetal (Grant 1978). The renewable character of the vegetable kingdom ensures a virtually unlimited supply of raw materials. They differ from type to type, but they all consist to a great extent of cellulose. The fibre structure gives paper not only its strength but also its comfortable feeling. Cotton contains approximately 95% cellulose, linen approximately 80% and wood approximately 45%. Grasses consist of only approximately 30% cellulose.

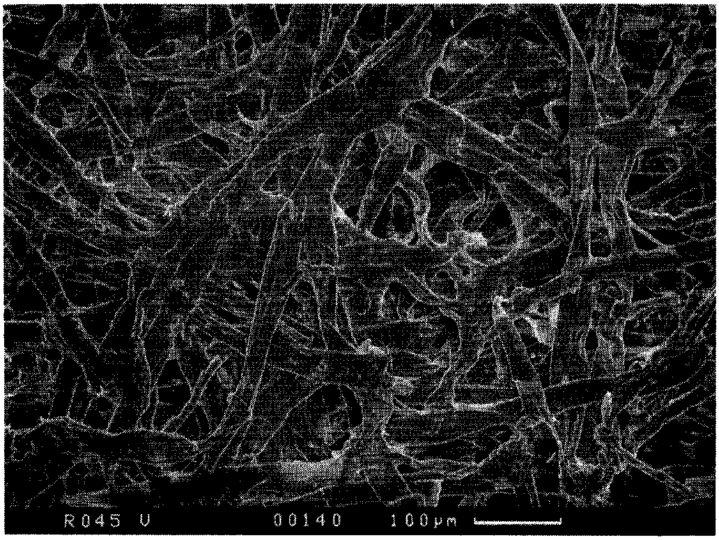


Figure 1.1 *Electron micrograph of the fibrous structure of paper made from softwood cellulose fibres (SEM micrograph by J. Timmner and J. Havermans)*

Other main components which give papers their identity are:

- fillers such as kaolin clay and calcium carbonate,
- optical brighteners for whiteness improvement, and
- starch derivatives as sizing agents.

Cellulose fibres used for papermaking can come from several sources but they are mainly derived from plants (Grant 1978). Some of these sources are:

- Bast fibres : flax, hemp, jute and ramie,
- Grasses : straw, bagasse, maize and bamboo,
- Leaf fibres : manilla and sisal,
- Seed hairs : cotton, and
- Wood fibres : softwoods (coniferous) and hardwoods (broad-leaved).

Although each fibre has its own characteristics and lends certain properties to the paper of which it is a component, economic considerations dominate. The main source of fibres for papermaking is wood. Some softwood species are pines such as the Norway pine (*Pinus resinosa* Ait.), spruces such as Norway spruce (*Picea abies* L.), and larches such as the European larch (*Larix decidua* Mill.). Hardwoods are for example birches (*Betula verrucosa*), eucalyptus (*Eucalyptus* spp.), beeches such as the American beech (*Fagus grandifolia* Ehrh.), poplars (*Populus* spp.), and oaks (*Quercus* spp.).

Softwood fibres are more than twice as long as hardwood fibres. There is also a chemical difference between the two types.

The papermaking process requires only the cellulose fibres and it requires separated fibres. Therefore the wood has to be pulped. "Pulping" is a term which embraces all the major operations to which the raw material is subjected between collecting the material and its conversion to pulp for the paper mill. Pulping is an international business. Traditional countries supplying woodpulp are Scandinavia, Canada and the USA. Nowadays this range is expanding to include Australia, Brazil, Portugal and Spain, all producing mostly eucalypt (Grant 1978).

In the wood cell-wall layers, the cellulose microfibrils are embedded in substances functioning as matrix, hemicelluloses, and encrusting material, lignin. The arrangement of these unordered polymers and microfibrils in the cell-wall layers varies greatly with plant species and is not known in detail. The three major wood polymers play different roles in the structure of the native fibre. The primary function of cellulose is to impart high tensile stiffness and strength to the tree. The role of lignin is to support the slender cellulose fibrils and prevent them from buckling, thereby giving the tree high compressive stiffness and strength. The function of hemicelluloses is less evident, but it has been suggested that they serve as a coupling agent or as an intermediate between cellulose and lignin. Since the wood pulp fibres provide stiffness and strength to the paper, the cellulose polymer is of primary importance for its mechanical properties. Therefore, the following section focuses on cellulose. Hemicellulose and lignin are only briefly mentioned.

1.5 Wood polymers

1.5.1 Cellulose

A number of aspects of cellulose structure still remain to be fully understood. Although everyone seems to agree on the molecular structure of cellulose, there is still some debate as to how the cellulose chains are arranged in the ordered regions and how the ordered regions are assembled into elementary fibrils, microfibrils, cell-wall layers and other cellulose morphologies. Part of the current knowledge of cellulose structure is reviewed in this section.

Molecular structure

Cellulose is a linear homopolysaccharide composed of β-D-glucopyranoside units linked by (1→4) bonds, Figure 1.2. Cellulose is one of nature's major building materials, found in algae (*e.g.* Valonia ventricosa), bacteria, plants and animals (tunicates). The molecular weight is high. Cotton cellulose has an average degree of polymerisation (DP) of about 10 000 (Golora, Iwanov 1953; Goring, Timell 1962), and wood cellulose about 8 000 (Goring, Timell 1962).

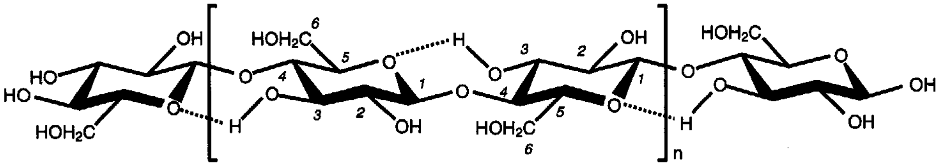


Figure 1.2 *The molecular structure of cellulose*

Supramolecular structure

At the supramolecular level, the cellulose chains are held together by strong intramolecular hydrogen bonds. The aggregates of cellulose chains may be ordered (crystalline cellulose) or unordered (amorphous cellulose). The ordered cellulose may crystallise in several different forms, polymorphs.

Polymorphism in crystallography refers to the situation in which a solid chemical compound or material exists in more than one crystalline form. The forms differ somewhat in physical properties such as solubility, melting point, density and crystal shape as well as in optical and electrical properties, although their solutions and vapours are identical.

The most common cellulose polymorph, is cellulose I. Two forms of cellulose I exist, cellulose I_α and I_β. Cellulose I_α is the dominant form in bacterial and algal celluloses and cellulose I_β is the dominant form in higher plants such as cotton and wood (VanderHart, Atalla 1984; VanderHart, Atalla 1987). Cellulose I can be transformed to cellulose II by alkali treatment, a process which is called mercerisation after its inventor Mercer in 1844. Cellulose II can also be formed by precipitation of dissolved cellulose (regeneration). A more detailed discussion on cellulose I is given below.
Other crystalline forms of cellulose may also be obtained through various treatments, but a discussion of this is beyond the scope of this chapter.

Cellulose I (I_α and I_β)

By infrared spectroscopy (Marrinan, Mann 1956; Marrinan, Mann 1958) and X-ray diffraction (Wellard 1954), it was early recognised that two forms of cellulose I exist in nature. The two forms were previously called cellulose I_β and I_α (Horii *et al.* 1987; Tanahashi *et al.* 1989; Yamamoto *et al.* 1989), but cellulose I_β is nowadays named cellulose I_α and cellulose I_α is denoted cellulose I_β (Atalla, VanderHart 1984; VanderHart, Atalla 1984; VanderHart, Atalla 1987; Wada *et al.* 1994). Cellulose I_α is thought to be biosynthesized by linear terminal complexes, and cellulose I_β by rosette-like terminal complexes (VanderHart, Atalla 1984; VanderHart, Atalla 1987). The ^{13}C-CP/MAS-NMR-signals from cellulose I_α and I_β have different chemical shifts and multiplicities, so the polymorphs are believed to have different chain conformations (VanderHart, Atalla 1984; VanderHart, Atalla 1987). Cellulose I_α and I_β may also differ in hydrogen bonding pattern, as revealed by Fourier transform infrared spectroscopy (Sugiyama *et al.* 1991a). Electron and X-ray diffraction show that cellulose I_α and I_β have different unit cells (Sugiyama *et al.* 1990; Sugiyama *et al.* 1991b). Cellulose I_α has a one-chain triclinic unit cell and cellulose I_β a two-chain monoclinic unit cell, see Figure 1.3.

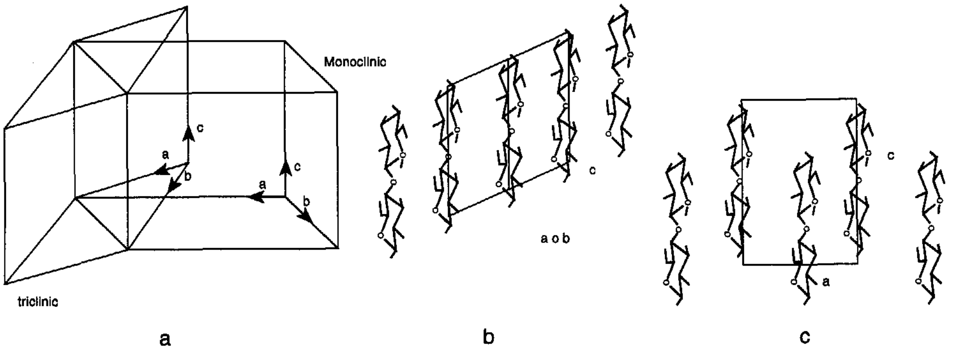


Figure 1.3 *The one-chain triclinic unit cell of cellulose I_α and the two-chain monoclinic unit cell of cellulose I_β (Sugiyama et al. 1991)*
(a) Relative orientation of unit cells
(b) Five cellulose chains in the cellulose I_α unit cell
(c) Five cellulose chains viewed along b of the cellulose I_β unit cell

Cellulose I_α is metastable and can be transformed to the more stable cellulose I_β by steam annealing, *i.e.* at high temperature and pressure, in alkaline or acidic solution (Debzi *et al.* 1991; Horii *et al.* 1987; Tanahashi *et al.* 1989; Wada *et al.* 1993; Wada *et al.* 1994; Yamamoto, Horii 1993; Yamamoto *et al.* 1989).

Cellulose I and II

The first models of the cellulose I and II structures were based on X-ray diffraction (Honjo, Watanabe 1958; Meyer, Misch 1937; Preston, Cronshaw 1958). The X-ray diffraction spots obtained from even the most ordered cellulose samples are comparatively poor, so that the knowledge of the atomic positions in the cellulose lattice is still incomplete. The current models of triclinic cellulose I_α and monoclinic cellulose I_β were discussed already, and the model of monoclinic cellulose II is shown in Figure 1.4. Several theories have been put forward to explain the differences between cellulose I and cellulose II. One theory suggests that cellulose I has parallel and cellulose II antiparallel cellulose chains in the unit cell (Kolpak, Blackwell 1976; Okano, Sarko 1985; Pertsin *et al.* 1984; Sarko, Muggli 1974).

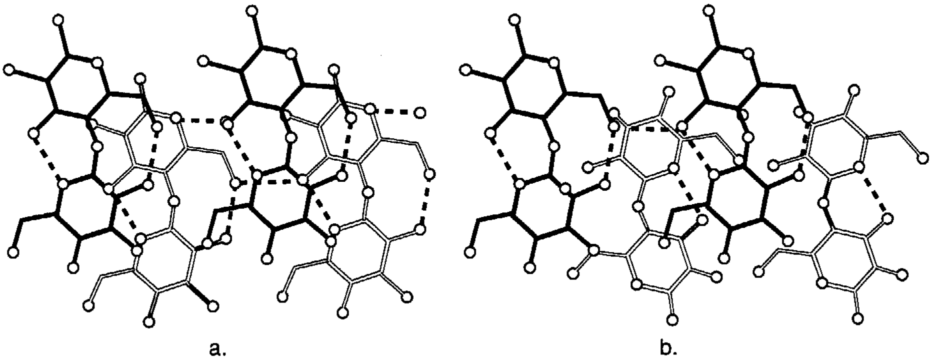


Figure 1.4 *Parallel (a) and antiparallel (b) packing at sheets of cellulose chains as seen in celluloses I and II, respectively (according to Young and Rowell, 1986)*

By labelling the reducing ends in Valonia cellulose (Hieata *et al.* 1984), bacterial cellulose (Kuga, Brown Jr. 1988) and cotton linters (Maurer, Fengel 1992), the chains in cellulose I were recently shown to be parallel. It has been suggested that the antiparallel mode of the chains in cellulose II is a result of chain folding (Kuga *et al.* 1993; Simon *et al.* 1988; Watanabe *et al.* 1974). Conformation analysis confirmed that folds in the cellulose chains are theoretically possible (Sarko 1976).

It has further been suggested that the differences between cellulose I and II result from differences in the conformation of the cellobiose units along the cellulose chains (Atalla 1981; Atalla 1989; Isogai *et al.* 1989; Kai, Xu 1991; Takahashi, Takenaka 1987; Turbak, Sakthivel 1990; VanderHart, Atalla 1983). These authors do not address the question of the chain polarity in cellulose I and II (parallel or antiparallel). The nature of the differences between cellulose I and II still remains to be fully explained.

Crystallinity

The cellulose lattice contains regions where the lattice is slightly disturbed and has a lower degree of order (amorphous cellulose). A large percentage of the unordered cellulose corresponds to the molecules on the surface of the elementary fibrils, which can account for a large proportion of the total cellulose, from a few percent in Valonia cellulose to more than 70% in plant primary wall cellulose (Chanzy 1990). A variety of methods exists to determine the degree of order of cellulose (the crystallinity), such as X-ray diffraction (Segal *et al.* 1959), NMR-spectroscopy (Teeäär *et al.* 1987) and infrared spectroscopy (Nelson, O'Connor 1964). The state of order can probably not be divided into two absolute parts as ordered or unordered; several degrees of intermediate or semicrystalline order exist. This may be the reason why different methods of determining the degree of order of cellulose give somewhat different values, *cf.* Jeffries *et al.* (1969).

Morphological structure

The aggregates of cellulose chains form elementary fibrils, and the elementary fibrils form microfibrils. The microfibrils are combined to greater fibrils and lamellae in the cell-wall layers, reviewed by Sjöström (1993). These organisational levels may be referred to as morphological structure.

Elementary fibrils and microfibrils

The smallest morphological units of ordered native cellulose are often called elementary fibrils, with diameters of about 35 Å (Blackwell, Kolpak 1976; Frey-Wyssling *et al.* 1966; Sarko, Muggli 1974). The cellulose elementary fibrils aggregate to form larger microfibrils with different sizes depending on the source of the material. The microfibrils in cotton vary in cross-section from 100 to 500 Å (Blackwell, Kolpak 1976).

How the cellulose chains are arranged in the elementary fibrils and microfibrils is not known in detail. Several theories exist, *e.g.* that the cellulose chain passes through several regions in the microfibrils where it is alternating between ordered and unordered cellulose phases, the fringed-micellar model (Mark 1940; Meyer, van der Wyk 1941). In another theory, the microfibrils consist of a single-phase, slightly imperfect cellulose I lattice; paracrystalline cellulose (Frey-Wyssling 1954; Kulshreshtha, Dweltz 1973; Shenouda, Viswanathan 1971). Using lattice imaging of algal, bacterial and cotton celluloses, a number of authors have recently suggested that the microfibrils are completely regular, *i.e.* that no fringed-micellar cellulose exists (Kuga, Brown Jr. 1987; Revol 1985; Sugiyama *et al.* 1985).

1.5.2 Hemicellulose

Hemicelluloses are heteropolysaccharides, built from miscellaneous monosaccharides, and have a degree of polymerisation of about 200 (Sjöström 1993). The proportion of hemicelluloses in wood is usually between 20% and 30%. The molecular structures of softwood galactoglucomannan and hardwood xylan are shown schematically in Figure 1.5. Most hemicelluloses are thought to be unordered.

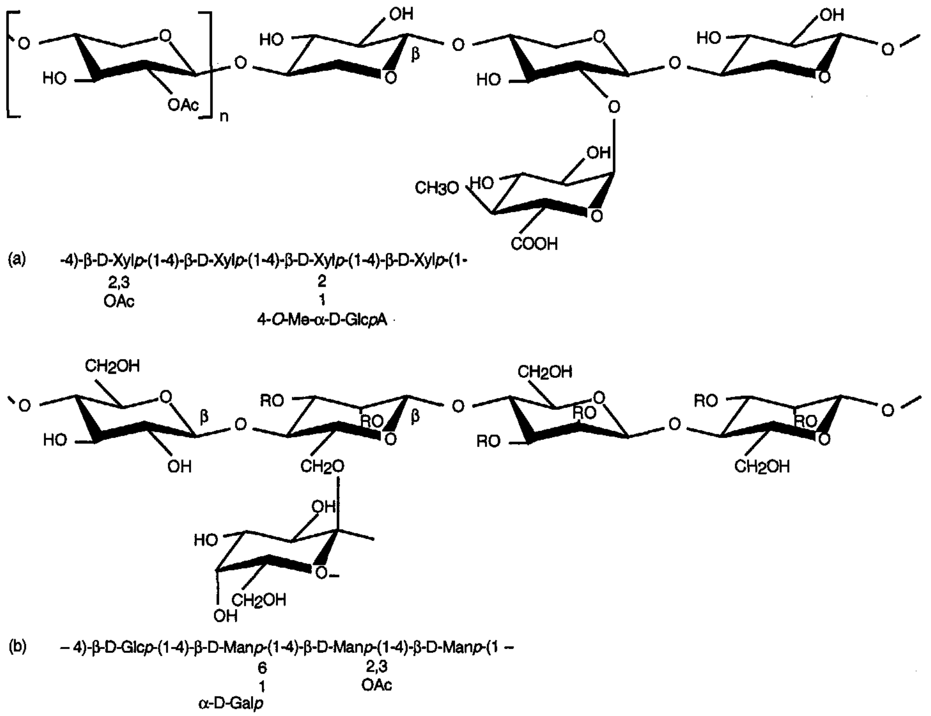


Figure 1.5 *The molecular structure of*
(a) hardwood xylan and
(b) softwood galactoglucomannan. After Sjöström (1993)

The following abbreviations are used here: R = CH_3O or H; (Glc*p*) glucopyranose, (Man*p*) mannopyranose, (Gal*p*) galactopyranose, (Xyl*p*) xylopyranose, and (Glc*p*A) glucopyranosyluronic.

1.5.3 Lignin

Lignins are polymers of phenylpropane units, Figure 1.6, with an average molecular weight of about 20 000 (Sjöström 1993). Normal softwood contains about 30% lignin, and normal hardwood about 25% lignin. Lignin is believed to be an unordered polymer.

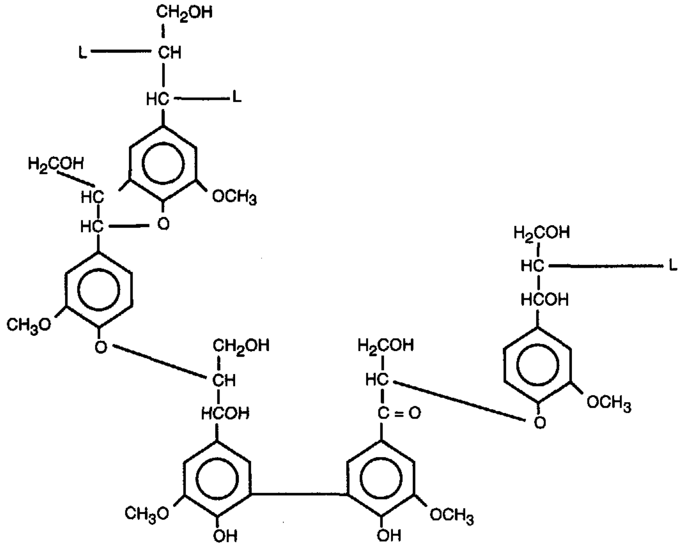


Figure 1.6 A structureal segment of softwood lignin. L- means continuation of the polymer. After Adler (1977)

1.6 Pulping, bleaching and papermaking

The pulping of wood fibres is a process which is still under development. This section briefly discusses some basic pulp materials and some general aspects of papermaking in order to provide more backgrounds concerning the papers used in the work described in this thesis.

1.6.1 Mechanical and chemical pulp

In general, mechanical pulp is produced from softwoods. In the original technique, logs of debarked wood are pressed with their long side parallel to the surface of a rotating grindstone while water is sprayed on the grinding zone. In addition to whole fibres, more or less damaged fibre fragments are torn off to produce a pulp that gives a paper with low-level mechanical properties. The pulp yield is in the range of 95–98%, *i.e.* almost all of the wood is converted into pulp. During most of the present century, such pulp had to be reinforced with stronger fibres in order to produce a paper of acceptable mechanical properties, as in the production of newsprint paper. This was also the kind of pulp used in the infamous machine-made paper during the second half of the 19th century, giving lignin-containing paper a very bad reputation among archivists and librarians. Later, another technique of mechanical pulping was developed that makes use of pressurised disk refiners to defibrillate wood chips, giving so-called thermomechanical pulps (TMP). In more recent developments, the wood chips are pre-treated with chemicals, resulting in high-quality mechanical pulps (CTMP) that are applied in many printing and writing papers today. No reinforcing fibres are needed with these pulps.

In chemical pulping, the cementing lignin is removed so completely that the wood fibres are easily liberated using only a mild mechanical treatment. There are two major chemical pulp processes, the sulphite and the sulphate or Kraft process. Sulphite pulping originated as an acid process using solutions of calcium hydrogen sulphite and sulphur dioxide. Acid sulphite pulps were the dominating chemical pulp from the last decade of the 1800's up to the 1950's. Later developments use magnesium bisulphite as a base, and the pH can then be increased to about 4–5. Sulphite pulps may be used to produce high-quality printing and writing papers, but mechanically the papers still have a somewhat brittle character. Sulphite pulping leaves much of the hemicelluloses in the fibres, with a pulp yield where approximately 55% of the wood is converted into pulp.

Kraft cooking is performed with a solution composed of sodium hydroxide and sodium sulphide. This pulp was harder to bleach than the sulphite pulps, but produced a strong and tough paper, and was therefore originally used mainly for brown packaging paper grades. The introduction of effective bleaching agents and multistage bleaching later made it possible also to produce high-quality printing and writing papers from Kraft pulps, and today Kraft pulps dominate in the production of such papers. Less hemicelluloses are left in the fibres than after sulphite pulping, resulting in a pulp yield in the range of 45–50%.

1.6.2 Bleaching of pulp

In order to increase the brightness of the paper, residual lignin has to be removed from the pulp in a bleaching process. Both mechanical and chemical pulps are bleached. In earlier

days, bleaching was performed by hanging the hand-made paper sheets on a clothes-line and exposing them to sunlight. Nowadays, chemical bleaching processes are used.
Traditionally, mechanical pulps were not bleached, but the high light-scattering power of the fine fibre fragments was utilised to produce a paper of reasonably high brightness. Today, most mechanical pulps used in printing and writing papers are bleached with hydrogen peroxide.
Chemical pulps are bleached in a multistage process, where an alkali-extraction is usually performed after each bleaching stage[1] in order to remove the excess of degradation products. Bleaching methods were improved sufficiently only after World War II, when new bleaching agents and multistage bleaching were introduced. One of the first multistage bleaching processes included an alkaline hypochlorite stage after the chlorination and extraction of pulp as described by Rapson (1956). During the years 1970–80, "conventional" bleaching processes usually consisted of six stages, with rather large amounts of chlorine in the first stage, followed by alkali-extraction, hypochlorite and chlorine dioxide. As a result of environmental concern, the use of elemental chlorine in modern bleach plants has been abandoned. A pre-bleaching stage with oxygen has been introduced, and the extraction stages have been reinforced with hydrogen peroxide and oxygen. The present trend is that chlorine dioxide should be eliminated from the bleach plant.

1.6.3 Papermaking

To the everyday user, paper may seem to be a homogeneous sheet material. Paper is, however, far from homogeneous. It is built up of at least a million components per gram, mainly fibres and filler particles. From an extremely disordered assembly of components, the papermaker manages to make a material that behaves in a homogeneous manner. If it were not for the fact that paper exists, this task would be considered impossible by any sensible engineer. Yet paper is today made in large quantities at a production rate unsurpassed in the manufacture of any other kind of material on a single process line.

Virtually all paper in mass-produced books has been made on a paper machine. From the mid-1800's, the old craft of hand-sheet papermaking could no longer provide sufficient amounts of paper for the production of books or office writing paper. Machine-made paper is produced as a continuous web, which gives the paper directional properties; the strength and stiffness in the machine direction generally being higher than those in the cross-

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[1] To describe the different bleaching sequences briefly special symbols are used which are given for example by Lorås (Casey, 1980).

machine direction. The raw materials for industrial papermaking include fibres that give the paper its mechanical stability, fillers that give optical properties and printability, and a multitude of chemical additives. The fibre material is generally wood-pulp fibres of mechanical or chemical origin, but cotton fibres in the form of linters or cotton cambers may also be used. The fillers are of inorganic origin, and include kaolin clay, calcium carbonate in the form of chalk or ground limestone, and specialty pigments like titanium dioxide that provide paper of high whiteness and high opacity. The chemical additives include hydrophobic agents that provide water and ink resistance, and starches or other water-soluble polymers that provide dry or wet strength *etc.*

From the mid-1800's up to about 1980, all machine-made paper was produced in an acid system. Water and ink resistance were imparted to the paper by the so-called rosin-sizing operation, in which papermaker's alum ($Al_2 (SO_4)_3 \cdot xH_2O$) is used to precipitate the rosin (the residue obtained after distilling of the turpentine from the gum of the southern pine) onto the fibre surfaces. The resulting paper is nowadays called acid paper. Since about 1980, however, the introduction of neutral sizing has meant that paper mills are gradually converting to neutral or slightly alkaline systems in their production of printing and writing paper. The use of a neutral process also enables to use calcium carbonate as a filler, a fact that made this changeover economically interesting to the papermaker. Almost all modern copy paper is therefore alkaline paper.

1.7 Paper degradation

1.7.1 Degradation types

The strength properties of paper depend on the quality of the cellulose fibres used (Dessauer 1989; Fellers *et al.* 1989; Lanting *et al.* 1985; Luner 1988; Samuelsson, Sörner 1990; Sjöström 1993; Young, Rowell 1986). In general, any degradation of long cellulose chains to shorter chains will lead to a reduction in strength. This can be summarised as follows:

> Cellulose may be degraded by hydrolysis or oxidation. Traces of metal ions, such as iron and copper together with SO_2 or NO_x promote the hydrolysis of cellulose. Cellulose may also be hydrolysed in an alkaline environment. Short-wave UV-radiation may break chains by photodissociation. Crosslinking reactions may make the cellulose structure stiff and brittle, thus increasing the likelihood that the chain breaks.

Under the influence of oxygen or light, lignin may degrade more rapidly than cellulose. Hemicellulose is hydrolysed more easily than cellulose and lignin.

1.7.2 Degradation mechanisms

The cellulose inside the microfibrils (ordered cellulose) is not as easily degraded as the cellulose at the surfaces of the microfibrils and in structurally weakened zones (unordered cellulose). From experiments using steam-explosion and acid hydrolysis, several degradation mechanisms have been suggested, as schematically illustrated in Figure 1.7.

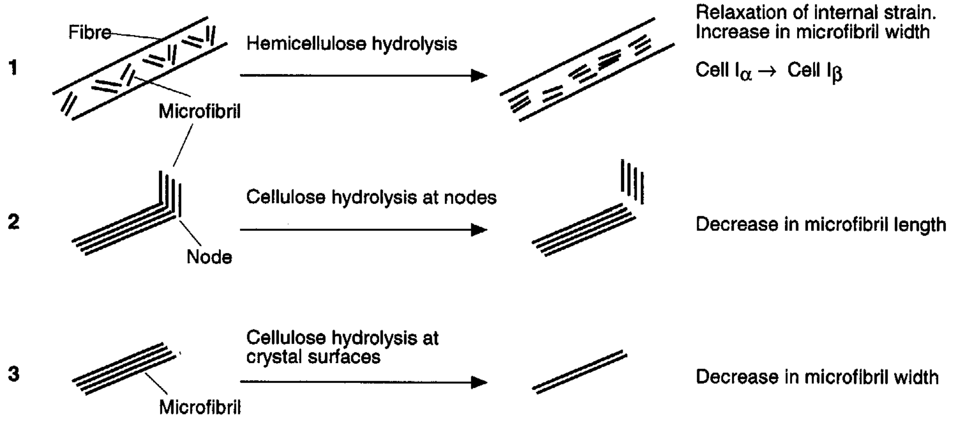


Figure 1.7 *The degradation mechanisms induced by steam-explosion and acid hydrolysis (Gurnagul et al. 1992; Tanahashi et al. 1989)*

(1) A partial hydrolysis of hemicellulose and unordered cellulose loosens the internal stresses in the ordered cellulose regions and results in a merging of the microfibrils, i.e. an increase in the microfibril width. At the same time, the high temperature affects the cellulose texture so that the metastable cellulose I_α transforms to cellulose I_β

(2) The microfibrils are preferentially cut at structurally weakened zones, nodes, leading to a decrease in the length of the microfibrils

(3) The surfaces of the microfibrils are hydrolysed, which decreases the width of the microfibrils. The relative increase in the amount of microfibril surface leads to a decrease in the degree of order of the cellulose

Since structurally weakened zones are more accessible in the water-swollen state, degradation by mechanism (2) in Figure 1.7 occurs in the enzymatic and liquid-phase hydrolysis of fibres. The degradation leads to a significant decrease in fibre strength and a decrease in the degree of polymerisation. Mechanism (3) in Figure 1.7 occurs during the vapour-phase hydrolysis of fibres and leads to only a moderate decrease in fibre strength (Gurnagul *et al.* 1992).

According to Young and Rowell (1986) the degradation of cellulose can be classified into two main routes:

1) reactions in which the end product is D-glucose (complete hydrolysis), and
2) reactions in which a range of products of low molecular weight are formed.

Normal ageing involves reactions such as oxidation, thermal oxidation, crosslinking and hydrolysis (Hon 1979; Young, Rowell 1986). All products formed can be determined separately or in combination thereof from measurements of for example the alkali-extractable fraction, the conductivity of cold-water extracts and the total organic compounds, as described in the annex.

Table 1.1 *Possible degradation reactions for cellulose*

Reaction	Involves	Products
Hydrolysis (thermal)	cellulose + H_2O	D-glucose
Acid-catalysed hydrolysis	cellulose + H_3O^+ (diluted)	D-glucose
Alkali-catalysed hydrolysis	cellulose + base	low-molecular weight products
Enzyme-catalysed hydrolysis	cellulose + cellulase	low-molecular weight products
Oxidation	cellulose + "O" (T, hv)	partially oxidised and depolymerised

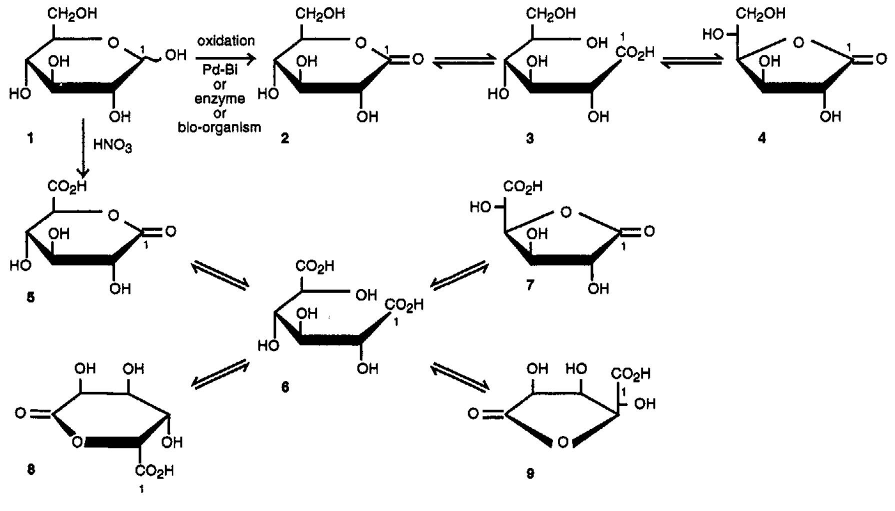


Figure 1.8 *The oxidation of D-glucose*

Oxidation and thermal oxidation of the primary alcohol group to an aldehyde and subsequently to a carboxylic acid on the C6 site may occur relatively rapidly. Oxidation of secondary alcohol groups at the C2 and C3 sites may also occur, initially leading to the formation of ketones. Further oxidation leads to ring splitting and the formation of carboxylic acids (Sjöström 1993). Thermal oxidation at room temperature and in the presence of light may break the glycosidic bond and cause depolymerisation (Blazej, Kosik 1985). Oxidation will be promoted when oxidation agents and/or metal ions *e.g.* iron and/or manganese, are present. With some polymers, *e.g.* carboxymethyl cellulose (CMC), oxidation with hydrogen peroxide or hypochlorite is applied to reduce the molecular weight somewhat, thus improving the biodegradability.

Besemer (1993) examined the reactivity of the structural features in an anhydroglucose unit towards the peroxide radical and found the reactivity sensibility sequence C6>C1=C4=C5>C2=C3.

Figure 1.8 shows two possibilities of oxidation of the D-glucose; a mild oxidation (pathway 1 to 2) leading to the formation of D-Gluconic acid (3) and its lactones (2 and 4), and a stronger oxidation (pathway 1 to 5) by which D-Glucaric acid (6) and its lactones are formed.

Sometimes peroxides are formed, and they can be strong oxidation agents resulting in radicals, especially in the presence of certain transition metal ions. These radical reactions can easily introduce carbonyl groups along the cellulose chains at the C6, C3 and C2 positions. After the formation of these carbonyl groups, chain cleavage can take place according to the so-called β-elimination. This reaction can take place fairly easily at several pH levels, but is especially rapid at pH levels higher than 8 (Luetzow, Theander 1974). Also C1 and C4 are liable to radical oxidation of the reactivity sequence given above. Such attack will generally lead to depolymerisation.

At high pH levels, monosaccharides as well as the end groups in polysaccharides will be converted to various carboxylic acids. (1→4)-Linked polysaccharides, including cellulose and most hemicelluloses are then degraded by an endwise mechanism, also called a peeling reaction. Figure 1.9 shows this reaction mechanism for the reducing end group of 1,4-β-D-glucan where the letter R represents the cellulose chain. The start of this reaction is the isomerization of the end group to a ketose in which the glycosidic bond is in the β–position. This structure is labile in alkali and therefore the glycosidic bond is cleaved and the end group is removed.

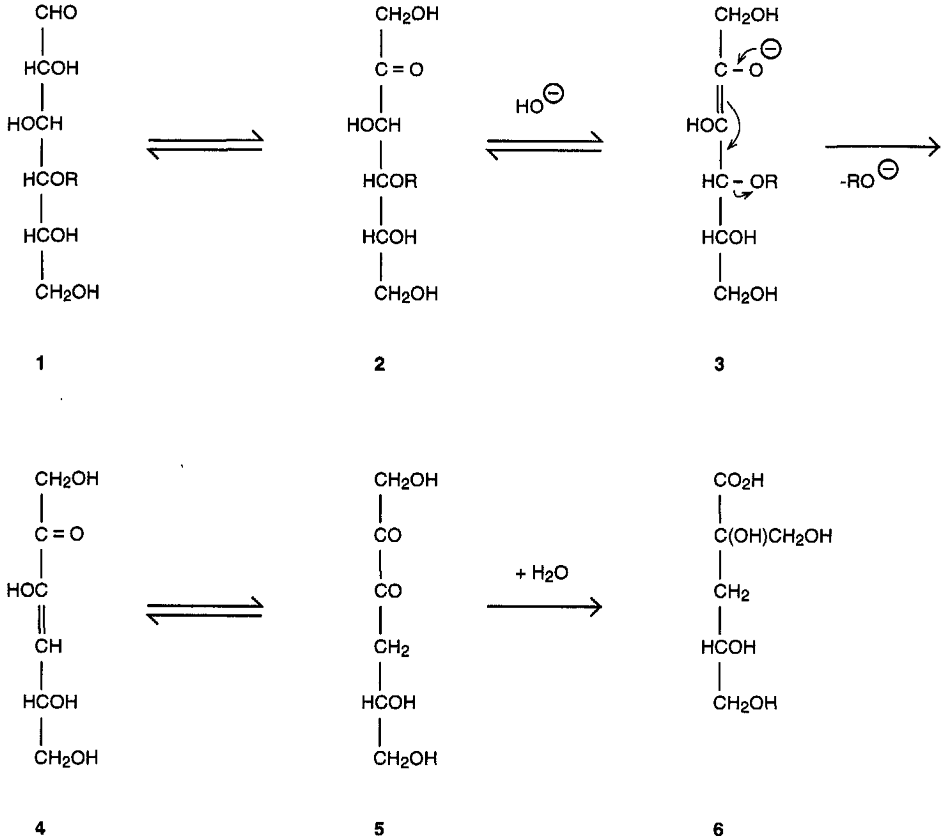


Figure 1.9 The endwise alkaline degradation ("peeling") of 1,4-β-D-glucan where the letter R represents the cellulose chain. Step 1→2 is the isomerization followed by 2→3 the enediol formation. Step 3→4 shows the β-alkoxy elimination where the cellulose chain is removed, followed by 4→5, tautomerization. Finally the benzilic acid rearrangement in 5→6 to epimeric 3-deoxy-2-C-hydroxymethylpentonic acids (isosaccharinic acids) takes place

Finally, thermal treatment, *e.g.* heating of cellulose using microwaves, will cause a ring closure-depolymerisation of glucans like starch and cellulose and this is in fact a preparative route for the synthesis of levoglucosan (Straathof *et al.* 1988), see Figure 1.10

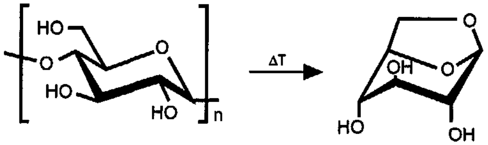
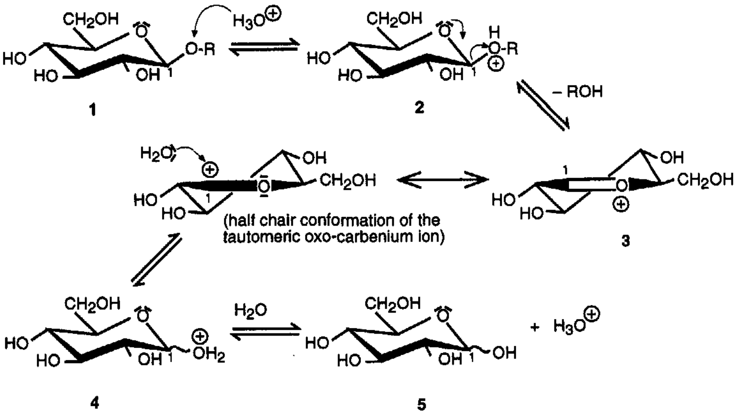


Figure 1.10 Deterioration of cellulose to 1,6-anhydro-β-D-glucose by thermal (microwave) treatment

One of the more expected degradation mechanisms is hydrolysis which generally results in chain scission and weakens the cellulose (Fengel, Wegener 1989; Flynn, Wilson 1958). Hydrolysis breaks the glycosidic bond. The principal molecular mechanism was proposed and confirmed by several researchers (Timell 1964; Timell 1965; Young, Rowell 1986) and is shown in Figure 1.11. In the first step, the proton of the catalysing acid reacts very rapidly with the glycosidic oxygen linking two sugar units. A so-called conjugate acid is formed (2). This step is followed by a slower step, the cleavage of the C-O bond yielding an intermediate cyclic oxo-carbenium ion (3). Finally, a conjugate acid is again formed and the proton is released (5). Acids can also influence the formation of anhydro-sugars *i.e.* levoglucosan from D-glucopyranose. Because of their greater accessibility to the acid, the amorphous regions of cellulose are first attacked. The acid catalysed hydrolysis of cellulose can be seen as a first order reaction, as described by Young and Rowell (1986). It was also concluded that the rate of hydrolysis of softwood cellulose is lower than that of hardwood cellulose.



R = polysaccharide unit

Figure 1.11 *A model for the acid-catalysed hydrolysis of cellulose, shown here for a non-reducing end group of cellulose*

Cross-linking is the formation of intermolecular bonds between cellulose chains. It results in the formation of ethers, esters, acetals and hemiacetals. Crosslinking limits water absorption and embrittles the structure (DuPlooy 1981; Meller 1961; Michie *et al.* 1961; Young, Rowell 1986).

The cause of the degradation of paper can be due to:

Degradation by internal factors

- Enhanced acid hydrolysis of cellulose occurs in the presence of a mineral acid (*e.g.* due to hydrolysis of the papermaker's alum and the pulping process used). This reaction may also be catalysed by metal ions in the paper. Water is of course required.
- Reactions occur between acid lignin monomers and cellulose (Bredenberg *et al.* 1989; Wong, Heremans 1988).

Degradation by external factors.

- Enhanced acid hydrolysis occurs due to the presence of acid-forming air pollutants such as sulphur dioxide (SO_2) and oxides of nitrogen (NO_x) together with water.
- Oxidation occurs in the presence of air pollutants such as ozone (O_3) and can be catalysed in the presence of metal ions.
- Photo-oxidation occurs due to UV radiation.
- Bio-deterioration occurs due to insects, mould *etc.*

In summary, it is clear that paper deterioration is a complex process where internal and external factors can stimulate each other, as can be seen in Figure 1.12, in which air pollutants play an important role.

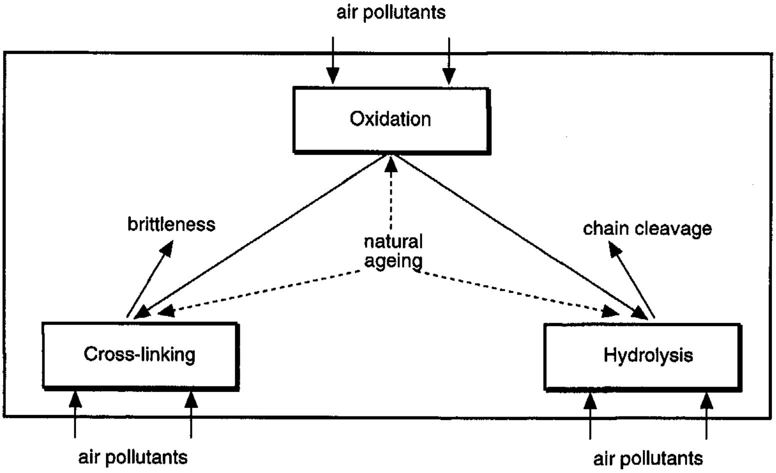


Figure 1.12 *A simplified overview of paper degradation*

1.8 Previous research projects on the effects of air pollutants

1.8.1 Which levels of air pollutants are to be used?

Table 1.2 shows a summary of all previous research projects known to us dealing with air pollutants and paper. The table was obtained using the literature reviews published in the Dutch ACBAM project (Lanting *et al.* 1985), the Swedish R&D-project on Paper Preservation report No. 1E (Fellers *et al.* 1989), and a separate literature search on reports published after 1985. The concentrations of the air pollutants are given in parts per million by volume (ppm).

Table 1.2 *Previous research projects studying the effects of air pollutants on paper deterioration (≈ stands for approximate and lab temp. for laboratory temperature, i.e. no exact temperature was given in the reference, RH is relative humidity)*

Year	Research by	Used pollutants level	SO_2 (ppm)	NO_x (ppm)	O_3 (ppm)	T (°C)	RH (%)
1931	Richter	low high	10 000 50 000	0 0	0 0	lab temp	lab level
1932	Kimberley	low high	2 9	0 0	0 0	30	65
1938	Jarrel *et al.*		8	0	0	≥50	lab level
1953	Langwell		≈5 000	0	0	lab temp	lab level
1956	Lyth Hudson, Milner	low high	≈5 000 ≈10 000	0 0	0 0	lab temp	≈50
1961	Lyth Hudson, Milner		5 000	0	0	lab temp	65 & 80
1964	Lyth Hudson *et al.*	low high	0.75 5 000	0 0	0 0	10 & 25	0 & 100
1968	Edwards *et al.*		≈ 10	0	0	25	60
1973	Atherton *et al.*		≈ 10	0	0	15 - 35	60
1988	Rodenburg	low high	≈ 60 ≈ 500	70 300	45 230	lab temp	lab level
1988	Havermans, Versluijs		≈ 0.8	0	0	23	50
1989	Daniel *et al.*		≈ 13	4	0	28	65 & 85
1990	Havermans	followed by thermal ageing	≈ 50	0	0	23	50
1990	Williams II, Grosjean		≈ 109	98	0	20	60
1991	Palm		≈ 153	213	0	23	40
1991	Iversen, Kolar	low high	500 10 000	0	0	22	30
1993	Banik *et al.*	low high	0.13 0.21	0.32 0.42	0 0	22	65

As can be seen in the table, the influence of air pollutants on paper was previously studied at many different levels of air pollutants. One of the first studies was carried out by Richter (1931). Only the influence of sulphur dioxide (SO_2) was studied. Later, other researchers carried out studies with SO_2 at concentration levels from 1 up to 10 ppm. One of the latest studies known, using only SO_2, was carried out by Havermans (1990). In this, not only exposure at a high level (50 ppm) was adopted, but the pollution period was followed by a thermal ageing period (3 days at 80°C and 50% RH).

All these studies were related to the high sulphur dioxide concentrations in the outdoor air due to industrial processes and combustion of coal and diesel oil. In several countries the SO_2 emission has decreased substantially. But not only sulphur dioxide is present in the air. Due to changes in industrial processes, and the increasing traffic the content of nitrogen dioxide (NO_2) in Europe is rising (Pederson *et al.* 1990). However in The Netherlands the NO_x emission is slowly decreasing (Reuvekamp 1995).
Only one study is known concerning the effects of nitrogen dioxide alone on paper (Iversen, Kolar 1991). High levels of 1-20 g/m^3 were used.

A few studies have been carried out using both nitrogen oxides and sulphur dioxide. The studies of Rodenburg (1988), Daniel (1990) and Williams II (1990) are the most recentenes. The researchers used high concentrations, 13 ppm SO_2 and 4 ppm NO_2 (Daniel *et al.* 1990), or ambient levels: 108 ppb SO_2 and 98 ppb NO_2 (Williams II, Grosjean 1990), 240 ppb SO_2 and 209 ppb NO_2 (Rodenburg 1988). The last known study was by Banik *et al.* (1993) also which authors applied ambient levels.

The question arises: –Do the ratios used, 3:1, 2:1 and 1:1 agree with reality? –. To answer this question, not only studies and monitoring of the outdoor pollution are useful, but also studies on the air quality in museums and archives.
First let us consider the outdoor situation. Two research projects are monitoring Europe: first the EMEP project, a co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe, and secondly, the ECE-programme concerned with long-term effects of air pollutants on stone and metals. This project has the advantage that most of the European large cities are monitored.
From interpreting these studies it can be concluded that the outdoor levels can be separated into a low-level range with the SO_2:NO_x ratio = 1:2 and a high-level range with the SO_2:NO_x ratio = 1:4. Here NO_x is the sum of NO and NO_2.

Until now, only one study is known describing the indoor air pollution in museums and archives (van der Wal *et al.* 1987). The authors found that the average ambient levels of air pollutants in the indoor air were approximately 5 ppb SO_2 and 10 ppb NO_x, *i.e.* a SO_2:NO_x ratio of 1:2. Some other important conclusions were also drawn:

- Summer pollution concentrations were lower than winter pollution concentrations (approximately 50%),
- NO_2 concentrations in the indoor air were lower than those in the outdoor air (outdoor approximately 40 ppb; indoor approximately 12 ppb),
- NO concentrations in the indoor air were higher than those in the outdoor air (outdoor approximately 30 ppb; indoor approximately 40 ppb), and
- the indoor air usually contains less SO_2 than the outdoor air (outdoor approximately 14 ppb; indoor approximately 6 ppb).

The main location of museums, libraries and archives is often in the city-centres, and in the locations the air pollution levels are relatively higher than in the countryside. The results of van der Wal (1987) showed also that the highest outdoor concentration levels were for SO_2 approximately 50 ppb and for NO_2 approximately 200 ppb (SO_2:NO_2 ratio = 1:4). In the results presented by CRCDG (Flieder, Daniel 1991), concentrations of approximately 28 ppb SO_2 and approximately 56 ppb NO_x (SO_2:NO_2 ratio = 1:2) were found in Paris (1990).

Another interesting point is the seasonal dependence of the concentration of air pollutants. In the Netherlands for example, the winter concentrations are higher than the summer concentrations. This effect was also observed in Paris in 1990 for the SO_2 levels, but not for the NO_2 levels. Probably enhanced coal combustion in water contributes.

In summary, the use of a SO_2:NO_x ratio = 1:2 can be used for experimental work for artificial pollution experiments.

It is important not only to look at ambient level concentrations but also to take higher levels into account. Of course, if we wish to follow a chemical process for many years, ambient levels are satisfying. This was also considered in the present work and levels from approximately 5 ppb SO_2 and 10 ppb NO_x were taken into account.

For the experimental part two methods were applied to enhance the reaction rates.

1. A thermal ageing stage was introduced after the artificial pollution in order to speed up the rate of reactions induced by the preceding pollution step.

2. The chosen level for the artificial pollution in Chapter 5, and Chapter 6, 20 ppm NO_x and 10 ppm SO_2, is a magnification of 1 000 times the nominal ambient level in order to speed up the saturation of paper by air pollutants.

1.8.2 Previous research projects, a review

This section focuses on the results of research projects carried out after 1985. For a summary of the results of earlier work, we refer to the two literature reviews in the Dutch ACBAM project (Lanting *et al.* 1985) and the Swedish R&D-project on Paper Preservation (Fellers *et al.* 1989).

First it should be noted that almost no research report pays attention to the composition of the papers used in the exposure experiments. Only a few researchers used well-defined materials such as pure cotton (*e.g.* Whatman filter paper) or hand-made sheets of pure bleached sulphite wood pulp. The use of such materials should be suitable for studying the degradation of cellulose, although the use of the filter paper may be questioned. It is for example known that the Whatman 42 filter paper undergoes a treatment with hydrochloric acid and hydrofluoric acid, by which the fibres are modified to improve the filtering capacity and to reduce the impurities left in the paper after production (Anonymous, 1962). Also, it is known that several filter papers are modified to improve their resistance against acid products like HNO_3. To study the effects of air pollutants on the deterioration of paper, the use of filter papers is therefore not recommended. Other materials that have been used were commercially available and it may therefore be argued that the material was defined through the production control. In some studies, however, the composition of the papers used was properly investigated.

Two recent deposition studies were performed by Rodenburg (1988) and by Banik *et al.* (1993). In the study by Rodenburg, papers were exposed to different levels of air pollutants (SO_2, NO_2 and O_3). He concluded that the deposition of SO_2 increased when $CaCO_3$ was present in the papers. Lignin-containing papers showed the highest deposition of the oxidative pollutants NO_2 and O_3. Long-term experiments showed an acidification effect, especially for the oxidative pollutants.

Banik *et al.* also used commercially available papers including some samples made from recycled fibres. All the papers were alkaline (pH > 9) and therefore contained an alkali reserve. It was not explained why these alkaline papers were also deacidified. These authors concluded that deacidification of alkaline papers increased the alkali reserve and that the absorption of SO_2 depended on the type of paper used. There was also some evidence that, after liquid-phase deacidification, the sizing of some papers was removed and that this might explain the greater absorption of air pollutants observed.

In summary, it is evident from these two studies that there is no advantage in deacidifying papers that are not acid. Not only the reactive sites brought in by the deacidification, but also damage of the papersurface by the treatment can cause an increase in the absorption of air pollutants. Moreover, care should be taken with the oxidative pollutants, since they react more strongly than the reducing pollutants.

After 1985, some studies were also carried out using SO_2 only. All investigators found that SO_2 reacts with the paper forming degradation compounds according to an acid-catalysed hydrolysis of cellulose. It was also found that alkaline papers took up more sulphur dioxide than acid papers. Using the precipitation reaction of the sulphates formed with barium ions (from barium nitrate), Havermans and Versluijs (1988) showed that an increase in the exposure time led to an increased absorption of sulphur in the paper samples. It was found that the uptake of SO_2 was higher in the acid papers than in the alkaline papers, which was surprising. The latest research known using SO_2 only was also carried out by present author in 1990. A higher concentration was used in this case, approximately 50 ppm. A new approach was the use of a deterioration cycle, involving a combination of a pollution over four days at 20°C and 65% RH, followed by thermal ageing for three days at 80°C and 65% RH. Long-term experiments over four weeks at 20°C and 65% RH and four weeks at 40°C and 65% RH were also performed. The author concluded that, under the conditions chosen, the thermal effect was higher than the pollution effect. There was an enormous decrease in strength properties after each deterioration cycle. Also it was shown that lignin-containing materials deteriorated more severely than pure sulphite pulp materials.

Only one study is known using NO_2 only. This was carried out by Iversen and Kolar (1991) within the framework of the Swedish R&D Project for Paper Preservation. In this work, only mechanical and optical properties were evaluated. These authors concluded that the measured properties of the neutral-sized papers were not affected by NO_2. This was not however the case for the acid-sized papers where a slight fibre modification was observed (relaxation effect), and it was suggested that the pollution of the acid papers led to a poor ageing stability. The mechanical properties of the lignin-containing papers were not affected, but a significant discolouration was observed.

In 1990, the work of Daniel *et al.* was published, and in the same year Williams II and Grosjean (1990) finished a similar project. Both projects used SO_2 and NO_2 together with deacidified papers. Later, Palm (1991) published a similar study. In general, all these authors found comparable results: an alkali reserve is preferable, although acid compounds are then absorbed more rapidly. The variation in the mechanical properties measured by Daniel *et al.* showed how difficult it is to draw conclusions based on mechanical properties only. Similar conclusions were reached by all these researchers. Palm also found that, depending on the type of paper, discolouration occurred and that there was no correlation between the rate of yellowing, the change in pH and the loss of strength properties. Williams II and Grosjean carried out chemical analyses and concluded that alkaline papers absorb more NO_2 than acid papers, and that the absorption capacity of the lignin-containing papers was the highest.

In summary, it was shown that the presence of lignin in paper promotes the absorption of SO_2. Alkaline papers absorb more NO_2 than do acid ones. In most cases, a deterioration was observed, although it was not always significant. Mechanical measurements only are not sufficient to prove paper deterioration at the starting level. Only NO_2 affects the papers in terms of fibre modification.

This thesis focuses on several particular items in the deterioration of paper and on the application of analytical techniques. Chapter 2 describes the application of infra-red spectroscopy to the study of the ageing of paper caused by the internal and external effects using different commercially available celluloses as well as a hand made paper. Chapter 3 continues the infra-red studies using an old and naturally aged paper. The effects of thermal deterioration in the presence and absence of oxygen is reported in chapter 4, while chapter 5 is focused on the effects of air pollutants (SO_2 and NO_x) using different paper grades. Finally, the contribution of deacidification using DiEthylZinc to the durability of paper is described in chapter 6.

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References

Adler, E. (1977).
Lignin chemistry. Past, present and future.
Wood Science and Technology 11: 169–218.

Anonymous (1962).
Der kleine Whatman Führer.
Whatman Filterpapier für das Laboratorium.
H. Reeve Angel Co. Ltd. London.

Atalla, R.H. (1981).
Spectroscopic studies of polymorphy in cellulose. A new structural model.
Second International Symposium on Wood and Pulping Chemistry, Stockholm, Sweden, 57–62.

Atalla, R.H. (1989).
Patterns of aggregation in native celluloses: implication of recent spectroscopic studies.
In: Cellulose, structural and functional aspects. (J. F. Kennedy, ed.), Ellis Horwood, Great Britain, 61–73.

Atalla, R.H.; D.L. VanderHart (1984).
Native cellulose: a composite of two distinct crystalline forms.
Science 223: 283-285.

Atherton, J.B.; F. Lyth Hudson; J.A. Hockey (1973).
The effect of temperature, light and some transitional metal ions on the sorption of sulphur dioxide by paper.
Journal of Applied Chemistry and Biotechnology 23: 407–414.

Banik, G.; W.K. Sobotka; A. Vendl; S. Norzcicsa (1993).
Effects of atmospheric pollutants on deacidified modern papers.
ICOM Committee for Conservation, Washington, 435–441.

Besemer, A.C. (1993).
The Bromine-Catalyzed Hypochlorite Oxidation of Starch and Inulin. Calcium complexation of oxidized fructans.
Thesis, Delft University of Technology.

Blackwell, J.; F.J. Kolpak (1976).
Cellulose microfibrils as disordered arrays of elementary fibrils.
Applied Polymer Symposia 28: 751–760.

Blazej, A.; M. Kosik, Ed. (1985).
Degradation reactions of cellulose and lignocellulose. Cellulose and its Derivatives. New York, John Wiley & Sons.

Bredenberg, J. B.; C. P. Masuka; A. Vouri (1989).
Thermal reactions of the bonds in lignin part II.
Holzforschung 43: 115–120.

Casey, J.P. (1980).
Bleaching.
Pulp and Paper, Chemistry and Technology, New York, Wiley-Interscience.

Chanzy, H. (1990).
Aspects of cellulose structure.
In: Cellulose sources and exploitation. (J. F. Kennedy, ed.), Ellis Horwood, 1–12.

Daniel, F.; F. Flieder; F. Leclerc (1990).
The effects of pollution on deacidified paper.
Restaurator 11: 179–207.

Debzi, E.M.; H. Chanzy; J. Sugiyama; P. Tekely; G. Exoffier (1991).
The I_α - I_β transformation of highly crystalline cellulose by annealing in various mediums.
Macromolecules 24: 6816–6822.

DePew, J.N.; C.L. Jones (1992).
A library, media and archival preservation glossary.
ABC-CLIO, Santa Barbara, California.

Dessauer, G. (1989).
Das Papier im Archiv.
Das Papier 43: 607–625.

DuPlooy, A.B.J. (1981).
The influence of moisture content and temperature on the aging rate of paper.
Appita 34: 287–292.

Edwards, C.J.; F. Lyth Hudson; J.A. Hockey (1968).
Sorption of sulphur dioxide by paper.
Journal of Applied Chemistry 18: 146–148.

Fellers, C.; T. Iversen; T. Lindström; T. Nilsson; M. Rigdahl (1989).
Ageing/Degradation of Paper. A literature Survey. Report No. 1E.
FoU-projektet för Papperskonservering, Stockholm, Sweden.

Fengel, D.; G. Wegener (1989).
Wood. Chemistry, Ultrastructure and Reactions.
Walter de Gruyter, Berlin.

Flieder, F.; F. Daniel (1991).
Annual Report 1991 of the STEP project CT 90-0100.
CRCDG, Paris, France.

Flynn, J.G.; W.K. Wilson (1958).
Degradation of cellulose in a vacuum with ultraviolet light.
Journal of Research of the National Bureau of Standards 60: 229–233.

Frey-Wyssling, A. (1954).
The fine structure of cellulose microfibrils.
Science 119: 80–82.

Frey-Wyssling, A.; K. Mühlethaler; R. Muggli (1966).
Elementary fibrils as structural elements of native cellulose.
Holz als Roh- und Werkstoff 24: 443–444.

Golora, O. P.; W. J. Iwanov (1953).
Über das Molekulargewicht der Cellulose.
Akademische Verlag.

Goring, D. A. J.; T. E. Timell (1962).
Molecular weight of native celluloses.
Tappi Journal 45: 454–460.

Grant, J. (1978).
Paper and boards manufacture. A general account of its history, processes and applications.
Technical Division, British Paper and Board Industry Federation, London.

Gurnagul, N.; D. H. Page; M. G. Paice (1992).
The effect of cellulose degradation on the strength of wood pulp fibres.
Nordic Pulp and Paper Research Journal 7: 152–154.

Havermans, J. B. G. A. (1990).
ACBAM Phase 5.1: Investigations on the accelerated ageing of paper under influence of sulfur dioxide.
PK 90.1008.
TNO, Delft, The Netherlands.

Havermans, J.B.G.A.; R.P. Versluijs (1988).
ACBAM Phase 2: The set up of an experimental pollution equipment. HI 88.1179.
TNO, Delft, The Netherlands.

Havermans, J.B.G.A.; J.P. van Deventer; R. van Dongen; F. Flieder; F. Daniel; P. Kolseth; T. Iversen; H. Lennholm; O. Lindqvist; A.S. Johansson (1994).
The Effects of Air Pollutants on the Accelerated Ageing of Cellulose Containing Materials - Paper.
EC/DGXII/STEP project CT-90-0100, BU3.94/1068/JH.
TNO, Delft, The Netherlands.

Hieata, K.; S. Kuga; M. Usuda (1984).
Electron staining of reducing ends evidences a parallel-chain structure in Valonia cellulose.
Biopolymers 23: 1807–1810.

Hon, D.N.S. (1979).
Photooxidative degradation of cellulose. Reactions of the cellulosic free radicals with oxygen.
Journal of Polymer Science 17: 441–454.

Honjo, G.; M. Watanabe (1958).
Examination of cellulose fibre by the low-temperature specimen method of electron diffraction and electron microscopy.
Nature 181: 326–328.

Horii, F.; H. Yamamoto; R. Kitamaru; M. Tanahashi; T. Higuchi (1987).
Transformation of native cellulose crystals induced by saturated steam at high temperatures.
Macromolecules 20: 2946–2949.

Isogai, A.; M. Usuda; T. Kato; T. Uryu; R.H. Atalla (1989).
Solid-state CP/MAS 13C NMR study of cellulose polymorphs.
Macromolecules 22: 3168–3172.

Iversen, T.; J. Kolar (1991).
Effects of nitrogen dioxide on paper. Report No. 5.
FoU-projektet för Papperskonservering, Stockholm, Sweden.

Jarrell, T.D.; J.M. Hankins; F.P. Veith (1938).
Deterioration of paper as indicated by gas chamber tests.
U.S. Department of Agriculture Technical Bulletin: 605.

Jeffries, R.; D.M. Jones; J.G. Roberts; K. Selby; S.C. Simmens; J.O. Warwicker (1969).
Current ideas on the structure of cotton.
Cellulose Chemistry and Technology 3: 255–274.

Kai, A.; P. Xu (1991).
Structure of alkali-swelling bacterial cellulose-brightener complex.
Polymer Journal 23: 1–6.

Kimberly, A.E. (1932).
Deteriorative effect of sulfur dioxide upon paper in an atmosphere of constant humidity and temperature.
US Bureau of Standards Journal of Research 8(February): 159–171.

Kolpak, F.J.; J. Blackwell (1976).
Determination of the structure of cellulose II.
Macromolecules 9: 273–278.

Kolpak, F.J.; M. Weith; J. Blackwell (1978).
Mercerization of cellulose. 1. Determination of the structure of mercerized cotton.
Polymer 19: 123–131.

Kuga, S.; R.M. Brown Jr. (1987).
Lattice imaging of ramie cellulose.
Polymer Communications 28: 311–314.

Kuga, S.; R.M. Brown Jr. (1988).
Silver labeling of the reducing ends of bacterial cellulose.
Carbohydrate Research 180: 345–350.

Kuga, S.; S. Tagaki; R.M. Brown Jr. (1993).
Native folded-chain cellulose II.
Polymer 34(15): 3293–3297.

Kulshreshtha, A.K.; N.E. Dweltz (1973).
Paracrystalline lattice disorder in cellulose. I. Reappraisal of the application of the two-phase hypothesis to the analysis of powder X-ray diffractograms of native and hydrolyzed cellulosic materials.
Journal of Polymer Science, Polymer Physics Edition 11: 487–497.

Langwell, W.H. (1953).
The permanence of paper: part 3.
Paper Board Makers Association Technical Bulletin 30: 2.

Lanting, R. W.; E.H.P. Logtenberg, J. Muetgeert, H. Nieboer and H.A. Westra (1985).
Veroudering en Aantasting van Cellulose door Luchtverontreiniging. R 88/195.
TNO, Delft, The Netherlands.

Luetzow, A.E.; O. Theander (1974).
6-aldehydo celluloses: thermal instability, beta-elimination, and acid hydrolysis.
Svensk Papperstidning 77: 312–318.

Luner, P. (1988).
Evaluation of paper permanence.
Wood Science and Technology 22: 81–97.

Lyth Hudson, F.; R.L. Grant; J.A. Hockey (1964).
The pick-up of sulphur dioxide by paper.
Journal of Applied Chemistry 14: 444–447.

Lyth Hudson, F.; W.D. Milner (1961a).
Atmospheric sulphur and durability of paper.
Journal of the Society of Architectorial Histories 2: 166–167.

Lyth Hudson, F.; W.D. Milner (1961b).
The permanence of paper. The use of radioactive sulphur to study the pick-up of sulphur dioxide by paper.
Paper Technology 2: 155–161.

Mark, H. (1940).
Intermicellar hole and tube system in fiber structure.
Journal of Physical Chemistry 44: 764–787.

Marrinan, H.J.; J. Mann (1956).
Infrared spectra of the crystalline modifications of cellulose.
Journal of Polymer Science 21: 301–311.

Marrinan, H.J.; J. Mann (1958).
Crystalline modifications of cellulose. Part II. A study with plane-polarized infrared radiation.
Journal of Polymer Science 32: 357–370.

Maurer, A.; D. Fengel (1992).
Parallel orientation of the molecular chains in cellulose I and cellulose II deriving from higher plants.
Holz als Roh- und Werkstoff 50: 493.

Meller, A. (1961).
The effect of crystalline structure on the alkaline degradation of cellulose fibres.
Journal of Polymer Science 51: 99–109.

Meyer, K.H.; L. Misch (1937).
The positions of the atoms in the new space model of cellulose. The constitution of the crystallized part of cellulose. VI. (in French).
Helvetica Chimica Acta 20: 232–244.

Meyer, K.H.; A.J.A. van der Wyk (1941).
Fine structure of cellulose fiber.
Zeitschrift für Elektrochemie 47: 353–360.

Michie, R.I.C.; A. Sharples; A.A. Walter (1961).
The nature of acid-sensitive linkages in cellulose.
Journal of Polymer Science 51: 85–98.

Nelson, M.L.; R.T. O'Connor (1964).
Relation of certain infrared bands to cellulose crystallinity and crystal lattice type. Part I. Spectra of lattice types I, II, III and of amorphous cellulose.
Journal of Applied Polymer Science 8: 1311–1324.

Okano, T.; A. Sarko (1985).
Mercerization of cellulose. II. Alkali-cellulose intermediates and a possible mercerization mechanism.
Journal of Applied Polymer Science 30: 325–332.

Palm, J. (1991).
Preventive and retrospective deacidification of paper. Report No. 6.
FoU-projektet för Papperskonservering, Stockholm, Sweden.

Pederson *et al.*, U. (1990).
Data report 1992. Part 1: annual summaries. 2/92.
NILU, Lilleström, Norway.

Pertsin, A.J.; O. K. Nugmanov; G.N. Marchenko; A.I. Kitaigorodsky (1984).
Crystal structure of cellulose polymorphs by potential energy calculations. 1. Most probable models for mercerized cellulose.
Polymer 25: 107–114.

Preston, R.D.; J. Cronshaw (1958).
Constitution of the fibrillar and nonfibrillar components of the walls of Valonia ventricosa.
Nature 181: 248–250.

Rapson, W.H. (1956).
The use of hypochlorite as a bleaching agent.
Tappi Journal 39: 284.

Revol, J.F. (1985).
Change of the d-spacing in cellulose crystals during lattice imaging.
Journal of Materials Science, Letters 4: 1347–1349.

Richter, G. (1931).
Durability of purified wood fibers. Accelerated ageing tests of various types of paper-making fibers.
Industrial and Engineering Chemistry 23: 371.

Reuvekamp, C. (1995)
Uitstoot verzurende stoffen daalt.
Chemisch Weekblad 18 februari 1995.

Rodenburg, L.J.M. (1988).
ACBAM Phase 4: Measurements of the depostition-rates of some cellulose containing materials. R 88/179A.
TNO, Delft, The Netherlands.

Samuelsson, M.L.; K. Sörner (1990).
Naturligt åldrat papper; Svenska papper 1908-1988. Report No. 4.
FoU-projektet för papperkonservering.

Sarko, A. (1976).
Crystalline polymorphs of cellulose: prediction of structure and properties.
Applied Polymer Symposia 28: 729–742.

Sarko, A.; R. Muggli (1974).
Packing analysis of carbohydrates and polysaccharides. III. Valonia cellulose and cellulose II.
Macromolecules 7: 486–494.

Schniewind, A.P.; R.W. Cahn; M.B. Bever (1989).
Concise Encyclopaedia of Wood & Wood-based Materials.
Pergamon Press, Oxford.

Segal, L.; J.J. Crealy; A.E. Martin Jr; C.M. Conrad (1959).
An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer.
Textile Research Journal 29: 768–794.

Shenouda, S.G.; A. Viswanathan (1971).
Crystalline character of native and chemically treated Egyptian cottons. I. Computation of crystallinity, disorder parameter, orientation factor, and spiral angle.
Journal of Applied Polymer Science 15: 2259–2275.

Simon, I.; L. Glasser; H.A. Scheraga; R.S.J. Manley (1988).
Structure of cellulose. 2. Low-energy crystalline arrangements.
Macromolecules 21: 990–998.

Sjöström, E. (1993).
Wood Chemistry. Fundamentals and Applications.
Academic Press, San Diego, California.

Straathof A.J.J.; H. van Bekkum; A.P.G. Kieboom (1988).
Preparation of 1,6-Anhydroglucose from (1-4)-Glucans using Microwave Technology.
Recuil des Travaux Chimiques des Pays-Bas 107: 647–648.

Sugiyama, J.; H. Harada; Y. Fujiyoshi; N. Uyeda (1985).
Lattice images from ultrathin sections of cellulose microfibrils in the cell wall of Valonia macrophysa Kutz.
Planta 166: 161–168.

Sugiyama, J.; T. Okano; H. Yamamoto; F. Horii (1990).
Transformation of Valonia cellulose crystals by an alkaline hydrothermal treatment.
Macromolecules 23: 3196–3198.

Sugiyama, J.; J. Persson; H. Chanzy (1991a).
Combined infrared and electron diffraction study of the polymorphs of native celluloses.
Marcromolecules 24: 2461–2466.

Sugiyama, J.; R. Vuong; H. Chanzy (1991b).
Electron diffraction study of the two crystalline phases occurring in native cellulose from an algal cell wall.
Macromolecules 24: 4168–4175.

Takahashi, M.; H. Takenaka (1987).
Transition of cellulose I family to cellulose II family.
Polymer Journal 19: 855–861.

Tanahashi, M.; T. Goto; F. Horii; A. Hirai; T. Higuchi (1989).
Characterisation of steam-exploded wood III. Transformation of cellulose crystals and changes in crystallinity.
Mokuzai Gakkaishi 35: 654–662.

Teeäär, R.; R. Serimaa; T. Paakkari (1987).
Crystallinity of cellulose, as determined by CP/MAS NMR and XRD methods.
Polymer Bulletin 17: 231-237.

Timell, T.E. (1964).
Wood hemicelluloses. Part I.
Advances in Carbohydrate Chemistry and Biochemistry 19: 247–302.

Timell, T.E. (1965).
Wood hemicelluloses. Part II.
Advances in Carbohydrate Chemistry and Biochemistry 20: 409–483.

Turbak, A.F.; A. Sakthivel (1990).
Solving the cellulose enigma.
Chemtech : 444–446.

Turner, S. (1991).
Which Paper?
Estamp, London.

van der Wal, J.F.; A.M.M. Moons; W.F. de Gids (1987).
ACBAM Phase 1: Research on the air quality in museums and archives. R 87/179A.
TNO, Delft, The Netherlands.

VanderHart, D. L.; R.H. Atalla (1983).
Studies of microstructure in native celluloses using solid-state 13C NMR.
TAPPI International Dissolving Specialty Pulps, TAPPI: 207–215.

VanderHart, D.L.; R.H. Atalla (1984).
Studies of microstructure in native celluloses using solid state 13C NMR.
Macromolecules 17: 1465–1472.

VanderHart, D.L.; R.H. Atalla (1987).
Further evidence for the coexistence of two crystalline forms in native celluloses.
ACS Symposium Series 340(Chapter 5): 88–118.

Wada, M.; J. Sugiyama; T. Okano (1993).
Native celluloses on the basis of two crystalline phase (I_α/I_β)system.
Journal of Applied Polymer Science 49: 1491–1496.

Wada, M.; J. Sugiyama; T. Okano (1994).
The monoclinic phase is dominant in wood cellulose.
Mokuzai Gakkaishi 40: 50–56.

Watanabe, S.; J. Hayashi; T. Akahori (1974).
Molecular chain conformation and crystallite structure of cellulose. I. Fine structure of rayon fibres.
Journal of Polymer Science 12: 1065–1087.

Wellard, H.J. (1954).
Variation in the lattice spacing of cellulose.
Journal of Polymer Science 13: 471–476.

Williams II, E.L.; D. Grosjean (1990).
Exposure of deacidified paper to ambient levels of SO_2 and NO_2.
Getty Conservation Institute, California.

Wong, P.T.T.; K. Heremans (1988).
Pressure effects on protein secondary structure and hydrogen deuterium exchange in chymotrypsinogen.
Biochimica et Miophysica Acta 1: 956.

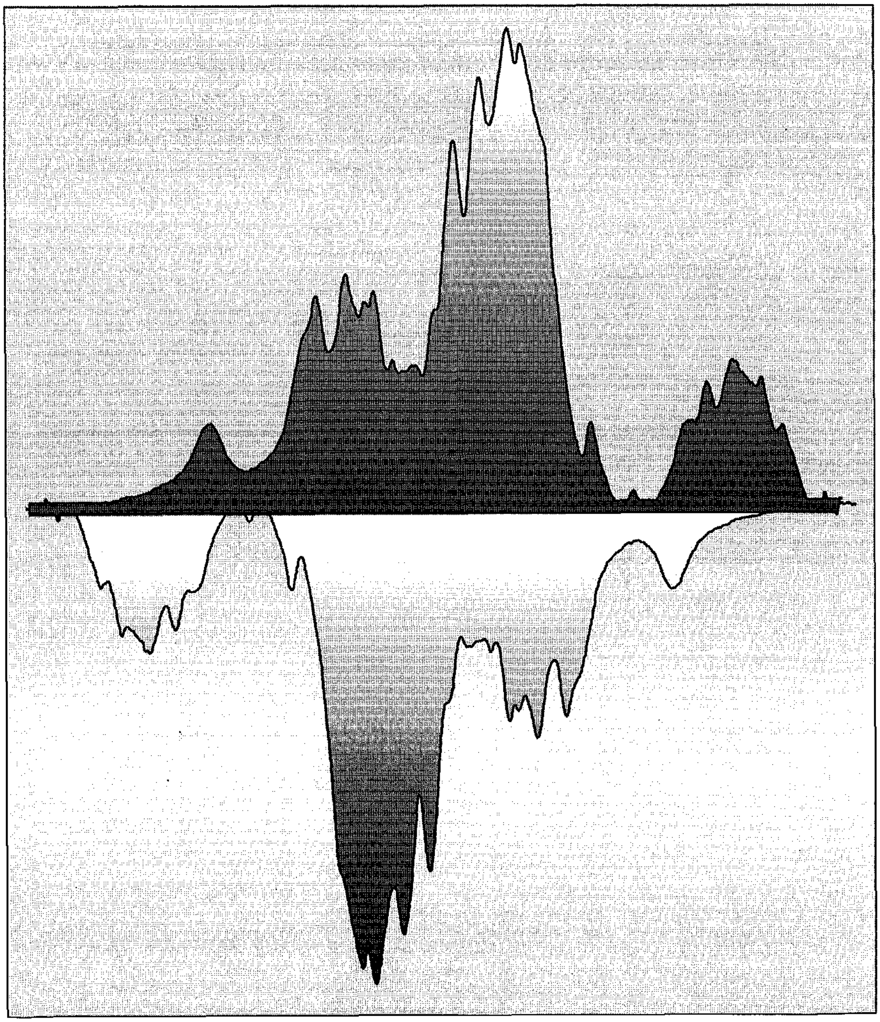
Yamamoto, H.; F. Horii (1993).
CP/MAS 13C NMR analysis of the crystal transformation induced for Valonia cellulose by annealing at high temperatures.
Macromolecules 26: 1313–1317.

Yamamoto, H.; F. Horii; H. Odani (1989).
Structural changes of native cellulose crystals induced by annealing in aqueous alkaline and acidic solutions at high temperatures.
Macromolecules 22: 4130–4134.

Young, R.A.; R.M. Rowell, Ed. (1986).
Cellulose. Structure, Modification and Hydrolysis.
New York, Wiley (Interscience).

2

Infrared spectroscopy as a tool for the characterisation of paper and paper deterioration



2. INFRARED SPECTROSCOPY AS A TOOL FOR THE CHARACTERISATION OF PAPER AND PAPER DETERIORATION

Summary

Fourier Transform Infrared Spectroscopy (FTIR) was used for the characterisation of paper and paper deterioration. Three commercial cellulose samples, one pulp sample and two lignin samples were analysed. These samples were, respectively, micro-crystalline cellulose (Sigmacell type 20 (S-3504), Sigma Chemical Company), native cellulose (Art. no. 2351, E. Merck, Darmstadt), Avicel cellulose (Art. no. 2352, E. Merck, Darmstadt), a beaten bleached sulphite softwood cellulose, a softwood lignin (Larch) and a hardwood lignin (Beech). From the bleached softwood cellulose, paper sheets were made and exposed to 50±5ppm sulphur dioxide for 8 weeks using a stainless steel cabinet. The conditions during the first four weeks were 20±1°C and 65±2% relative humidity (RH). Samples were taken at the end of this period. During the next four weeks the conditions were: 40±2°C and 65±5% RH.

In order to study morphological changes in the cellulose, the crystalline fraction in the cellulose was determined using the crystallinity index (CI). The CI was calculated by dividing the intensity of the absorbance band of the CH_2 bending vibrations (1372 cm^{-1}) by the intensity of the band of the CH_2 stretching vibration (2900 cm^{-1}) in cellulose. Deuterium exchange experiments were also carried out by exposing the cellulose to a saturated vapour of D_2O (4 hours, room temperature).

The IR techniques used were transmission spectroscopy under vacuum using KBr discs, Diffuse Reflectance Spectroscopy, Attenuated Total Reflectance spectroscopy and infrared microscopy. Besides FTIR spectroscopy, chemical and mechanical analyses were performed.

From reflectance spectroscopy, it was concluded that reproducible spectra are hard to obtain using Attenuated Total Reflectance, due to the elastic form of the cellulose fibre.

From transmission spectroscopy, it was concluded that the use of KBr discs gives a high reproducibility (1 mg sample in 300 mg KBr). The reproducibility of the spectra using the IR-microscope depends on the selected fibres. Each fibre may contain contaminations that become visible at the microscopic level. However, together with the other techniques, it provides an important contribution to the characterisation of fibrous materials.

Infrared spectroscopy makes an important contribution to the characterisation of cellulose morphology. Lignin can be detected and a distinction can be made between hardwood and softwood lignin at levels where normal microscopic fibre determinations are inadequate. Hemicellulose can be detected by its band at approximately 815 cm^{-1}. The presence of this band also indicates that the cellulose was derived from wood.

It may be concluded that SO_2 increases the crystallinity of cellulose at 65% RH. The use of the CI can therefore be a test to monitor the paper acidification by its change in texture. Although an increase in temperature leads to more reactive aldehyde and/or keto groups as measured by the copper number, this was not revealed in the spectra. It is therefore suggested that cellulose exposed to SO_2 will form hydrocellulose, which has a higher reducing power in a (boiled) solution than in its solid state.

2.1 Introduction

The objective of this study was to determine to what extent infrared spectroscopy can contribute to the characterisation of paper and paper ageing. This chapter describes the application of infrared spectroscopy to different samples of cellulose and lignin, and includes an interpretation of infrared spectra in relation to the deterioration of paper. The study was a part of the Netherlands research program on paper preservation, known as the ACBAM project[1], a long-term research program carried out by the Netherlands Organisation for Applied Scientific Research, TNO, and commissioned by the Dutch Ministry of Welfare, Health and Cultural Affairs.

Paper is a fairly random network consisting mostly of cellulose fibres. The structures of the network and the length of the fibres determine the physical and mechanical properties of the paper (Fengel and Wegener 1989). Depending on the time at which the paper was manufactured, additives will have been used, fillers such as clay, sizing such as alum-rosin and/or coatings such as starch. If wood was the raw material for the production of the cellulose fibres, the paper may contain both lignin and hemicellulose (Nassar and MacKay 1984; Lanting, Logtenberg *et al.* 1985; Sjöström 1993).

Research on paper ageing is mostly based on accelerated ageing tests. At high temperatures and humidities, the deterioration process of paper is simulated and accelerated. Ageing leads to changes in chemical, physical and mechanical properties (Havermans, van Deventer *et al.* 1994). Chemical changes can be detected by infrared spectroscopy. IR spectroscopy of cellulose has been used since the '50s (Brown, Holliday *et al.* 1951), but this technique was not applied to sheets until some 30 years later (Hon 1984).

A literature search by the TNO Centre for Information and Documentation showed that there is little literature available about infrared spectroscopy and paper. However, there is a relatively large body of information available regarding the infrared spectroscopy of cellulose and, particularly in the past five years, of wood. As paper is made mostly from wood pulp, this section will concentrate on wood cellulose and wood components like lignin.

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[1] ACBAM is an abbreviation for "onderzoek naar de mate van Aantasting van Cellulose- en ligninehoudende materialen in relatie tot de concentratie van luchtverontreinigende verbindingen in Nederlandse Bibliotheken, Archieven en Musea"

Cellulose has been studied by Marrinan and Mann (1954 and 1956). They concentrated on determining the texture (crystallinity) of cellulose. Deuterium oxide (D_2O) was used to replace bound water (Marrinan and Mann 1954; Marrinan and Mann 1956; Marrinan and Mann 1956; Marrinan and Mann 1956). Concomitantly partial OH/OD exchange occurs. The amorphous domains are readily accessible to water whereas the crystalline parts are not. The accessibility to water and to D_2O, is therefore a measure of the ratio of amorphous to crystalline cellulose. In the infrared spectrum, the -O-D bond can be detected at approximately 2500 cm^{-1} (νOD). The authors concluded that:

- The cellulose fraction in which exchange (mainly $H_2O \rightarrow D_2O$) has not occurred after four hours at room temperature may be regarded as crystalline,
- All OH groups in crystalline cellulose are bound by hydrogen bridges,
- OD absorption in the amorphous region is observed as a broad band originating from the exchanged water,
- A discrete number of H bridges of defined strength in the crystalline area of cellulose results in a specific number of transmission bands.

Furthermore, Marrinan and Mann recognised that two forms of cellulose type I exist.

Nelson and O'Connor (1964) undertook similar experiments and concluded that a clear distinction can be made between the various forms of crystalline cellulose. The shifts in the OH and OD stretching vibrations in the spectrum that occur after treatment with deuterium oxide provided a consistent pattern. This supported the conclusions drawn by Marrinan and Mann. Nelson and O'Connor (1964) established a relationship to rank cellulose from various sources, based on the extent of crystallinity (Nelson and O'Connor 1964; Nelson and O'Connor 1964). The ratio between two defined bands was determined for some 10 cellulose samples. These were the CH_2 bending vibrations (1372 cm^{-1}) and the CH_2 stretching vibration in cellulose (2900 cm^{-1}). The observed ratio was compared with the intensity of the 002 reflection in the X-ray powder diffraction diagram which is a measure of the crystallinity of the cellulose. Higgins, Steward and Harrington (1961) demonstrated typical differences between the two anomeric bonds in glucose (Higgins, Stewart *et al.* 1961).

Difference in the anomeric bond

Barker *et al.* investigated some derivatives of D-glucopyranose especially with respect to the configuration of the anomeric bonds in the infrared spectrum (Barker, Bourne *et al.* 1953; Barker, Bourne *et al.* 1954). The authors identified the characteristics of the *α- and the β-anomeric bonds.* The axial position of the anomeric OH-group in the most stable

chair conformation of β-glucopyranose leads to van der Waals interaction with the axial hydrogen atom on C3 and C5. As a result, the frequency of the C1-H deformation vibration of *α- and β-glucopyranose* differs. The α-anomer of glucopyranose has a transmission band near 11.8 μ (847 cm^{-1}) and the β-anomer has a band near 11.2 μ (893 cm^{-1}).
Other researchers showed that cellulose type I (ring vibration) band at 10.9 μ (917 cm^{-1}) is most apparent in the β-glucopyranose-anomer (Higgins, Stewart *et al.* 1961; Zhbankov 1966; Nassar and MacKay 1984; Sjöström 1993).

In a combined infrared and electron diffraction study of 10 cellulose samples, Sugiyama *et al.* confirmed that native cellulose exists in two phases, I_α (triclinic state), and I_β (monoclinic state). The conversion of I_α to I_β can be achieved for example by intra-crystalline swelling followed by deswelling and by a hydrothermal treatment in the presence of NaOH. Furthermore a distinction may be made between two families of native cellulose: Family I where mainly the monoclinic phase I_β is present and family II where both phases are present, I_α and I_β. I_α can be identified by a band near 750 cm^{-1}, while I_β can be identified by the 710 cm^{-1} band (Sugiyama, Persson *et al.* 1991; Sugiyama, Vuong *et al.* 1991).

Effect of the degree of polymerisation

The β(1→4) dimer, oligomers and polymers have been investigated spectroscopically by Higgins *et al.* (1961) and Zhbankov (1966). On the basis of deuterium-exchange experiments (OH→OD), these authors assumed that the ratio of the fraction of non-exchanged OH (approximately 3500 cm^{-1}) to the OD fraction (approximately 2500 cm^{-1}) provides a measure of the degree of polymerisation. Bouchard (1990), however, reported that the degree of polymerisation of cellulose could not be determined by IR spectroscopy. On the other hand the acid catalysed hydrolysis could be monitored (Bouchard, Garnier *et al.* 1990).

The IR spectroscopy studies on wood, pulp and paper had mainly the following aims:

- To distinguish between hardwood and softwood (Michell, Watson *et al.* 1965; Durig, Esterle *et al.* 1988; Michell 1988; Owen and Thomas 1989),
- To identify the origin of wood species,
- To recognise the early stages of fungal attack on wood (Gibson, Krahmer *et al.* 1985),
- To identify the pulp and delignification processes,
- To identify deterioration processes in pulp and paper.

The links between the various IR absorption bands and the different wood components are also discussed in the literature. Sometimes there are conflicts between the various studies. Fengel (1989) described the application of IR spectroscopy to various components of wood such as cellulose and lignin. The degree of crystallinity of cellulose can be determined effectively by IR or FTIR spectroscopy, but there is no clear information about the reproducibility of the results (Nelson and O'Connor 1964; Fink and Phillip 1985; Fengel and Wegener 1989).

The spectra of softwood and hardwood lignin are different, due to the different ratios of guaiacyl, syringyl and p-hydroxyphenyl units in these two types of lignin (Faix, Patt *et al.* 1987; Faix 1988). The various saccharides (hemicellulose and cellulose) and other compounds specific for certain types of wood can also be identified.

Kuo *et al.* (1988) described the application of photo-acoustic spectroscopy, *PAS*, in a study concerning wood attack by brown fungi (Kuo, McClelland *et al.* 1988). An important result is the correspondence between PAS spectra and spectra obtained by transmission infrared spectroscopy with KBr discs. With FTIR, wood deterioration caused by brown fungi was identified at an earlier stage than with conventional methods like microscopy, or weight loss examination. The identification of attack by brown fungi is generally based on the increase in carboxylic acid groups (1750 cm^{-1}).

There has been extensive research into the quantification of lignin in pulp (Marton and Sparks 1967; Schultz, Templeton *et al.* 1985; Faix 1988). The aromatic nature of lignin can be detected at, for example, 1500 cm^{-1}. The intensity of this band compared with the aliphatic part of the spectrum is a measure of the proportion of lignin in the pulp. It has been demonstrated that the determination of lignin with IR or FTIR spectroscopy is much faster than wet chemical analytical methods. Transmission spectrometry in KBr provides the most reliable results. Transmission spectroscopy of wet pulp using a circular cell also provides acceptable results. Reflection spectroscopy of solids such as sheets of paper is currently under investigation. The diffuse reflectance infrared Fourier transform *(DRIFT)* accessory and other equipment is only occasionally used for paper and pulp materials. However, the researchers concerned are optimistic about these techniques (Hon 1984; Faix, Patt *et al.* 1987; Faix 1988).

The application of attenuated total reflectance *(ATR)* spectroscopy has provided the least reliable results. As paper is a compressible material (Marton and Sparks 1967; Kuo, McClelland *et al.* 1988) there will be a poor contact area between the measurement crystal and the paper. Therefore also the spectrum will be poor.

The application of infrared spectroscopy to study paper ageing has been described amongst others by Kleinert (1969), Hon (1984), Banik (1983), Hemmingson and Wong (1989). Kleinert used FTIR and IR to investigate the photo-oxidative degradation of paper (Kleinert 1969), focusing on the carboxylic acid groups that were formed. Kleinert did not observe bands at 1735 cm^{-1} or 1600 cm^{-1}, but he found a difference in intensity at 1640 cm^{-1} between the aqueous extracts of the original material and those of the oxidised product. Zhbankov (1966) and others had demonstrated earlier that this band is due to absorbed water (Zhbankov 1966). Hon also investigated the photo-oxidative decay (UV radiation) of paper and concluded that the radiation results in the formation of carbonyl, carboxylic acid and hydroperoxide groups in the cellulose polymer (Hon 1979; Hon 1984). It was also found that the effects on paper of gases such as SO_2 and NO_2 can be detected by IR or FTIR whereas Banik concluded that exposure of unpigmented paper to SO_2 and light does not result in significant changes in the infrared spectrum (Banik and Ponahlo 1983).

Hemmingson and Wong (1989) studied the photo-oxidative degradation of newsprint by exposing it to direct and indirect (shade) sunlight. After 8.5 months, the paper was extracted with a water/acetone mixture and the extracts were analysed with IR and FTIR (liquid between KBr pellets) and NMR. After exposure to direct sunlight, fatty acid compounds were detected in the aqueous extract, along with lignin and sugar fragments. No sugar fragments were found after exposure to indirect sunlight. One of the dominant monomeric products found was vanillic acid, 4-hydroxy-3-methoxybenzoic acid.

In summary different forms of cellulose can be distinguished using infrared spectroscopy, *e.g.* types I, IIb and III by observing the β-anomer bands at approximately 920, 894 and 766 cm^{-1} respectively. Furthermore the occurrence of the α-anomer and the β-anomer in the glucopyranose-anomer can be distinguished. The α-anomer has a transmission band at approximately 845 cm^{-1} and the β-anomer has a band at approximately 890 cm^{-1}. Also the occurrence of amorphous and crystalline cellulose can be observed. This is indicated for example by the ratio of the 1372 to the 2900 cm^{-1} band-intensities.

Native cellulose is generally obtained from cotton fibre which is composed entirely of Cellulose I_β (Atalla and VanderHart 1984; VanderHart and Atalla 1984; VanderHart and Atalla 1987), thus paper made mainly of cotton consists of cellulose type I. The bands at approximately 710, 894 and 920 cm^{-1} in the infrared spectrum should therefore be present. Native cellulose is used in this research project as a reference. Zhbankov (1966) has provided an extensive discussion of cellulose spectra, which in combination with other literature references, are here used to interpret cellulose spectra.

In this chapter, the experimental set-up is first described. Subsequently the IR-data for six different materials four commercial cellulose and two lignin materials, are reported and discussed. Finally the IR spectra of cellulose upon exposure to sulphur dioxide are described and discussed.

2.2 Experimental

2.2.1 Materials used

Commercial model materials as well as fibres from handmade paper were used. These are listed in Table 2.1. Unless otherwise specified, all materials were of analytical grade (pro analysis).

Table 2.1 *Investigated materials*

Name	Description and source
paper hand sheets (bleached sulphite softwood cellulose)	Paper hand sheets (80 g/m^2) made at TNO consisting of bleached sulphite softwood cellulose. The fibres were beaten to 30° in a Hollander. Demineralised water was used for pre-treatment and sheet forming. The sheets of paper were dried at 70°C for 1 hour and then stored in the dark at 23°C and 50% RH.
Cellulose (micro-crystalline)	Sigmacell type 20 (S-3504), Sigma Chemical Company [1]
Cellulose (native)	Art. no. 2351, E. Merck, Darmstadt[1]
Cellulose (Avicel)	Art. no. 2352, E. Merck, Darmstadt[1]
Softwood lignin	Larch lignin. Supplied by O. Faix of the Bundesforschungsanstalt für Forst- und Holzwirtschaft
Hardwood lignin	Beech lignin. Supplied by O. Faix of the Bundesforschungsanstalt für Forst- und Holzwirtschaft

[1] Neither Sigma nor Merck gave information about the source of the raw materials used for their cellulose.

2.2.2 Equipment and applications

The IR equipment used is described in Table 2.2.

Table 2.2 *Equipment used and its parameters*

Equipment	Application and or parameters
Bruker 113v FTIR	TGS[1] or nitrogen cooled MCT[2]
Detector	4000 - 400 cm^{-1} (25 mm to 2.5 mm)
Range	2 cm^{-1}
Resolution	vacuum
Operating pressure	64 (transmission spectroscopy)
Number of scans	250 (reflection spectroscopy)
Spectra-Tech IR-Plan analytical microscope	Linked to Bomen MB100 FTIR
Magnification	187 x
Detector	nitrogen cooled narrow band MCT
Range	4000 - 750 cm^{-1} (13 mm to 2.5 mm)
Resolution	4 cm^{-1}
Operating pressure	atmospheric
Number of scans	100 (unless otherwise specified)

[1] TGS detector stands for triglycine sulphate pyroelectric detector
[2] MCT detector stands for mercury cadmium telluride detector

All spectra were reproduced using Spectra-Calc software of Galactic Industries Corporation (version 2.1) (Software 1990).

IR-Transmission spectroscopy in KBR

For the powder samples, approximately 1 mg was mixed with 300 mg KBr (Merck, spectroscopic grade). For the paper samples, about 1 mg of paper was scraped with a scalpel from the surface of the sheets of paper. This material was mixed with about 300 mg KBr. In both cases the mixture was transferred to a die and pressed to a KBr pellet using a pressure of 8 to 10 tonnes. All transmission measurements were carried out at least in duplicate under vacuum.

IR-reflectance spectroscopy

All spectra were recorded under vacuum. The attenuated total reflectance (*ATR*) spectroscopy was carried out with an internal reflection element (IRE) made of KRS-5, a synthetic mixed-crystal thallium bromide iodide. Two sheets of paper were clamped in the internal reflection element. A torque wrench was used to tighten the element to a torque of 25 units. Diffuse reflectance (DRIFT) spectroscopy was applied to material scraped from sheets of paper. Approximately 0.5 mg of scraped material was mixed with about 200 mg of KBr and placed in a DRIFT cell. Reflectance spectroscopy was also applied directly to an 80 by 80 μm area of the paper to be analysed. This area was selected with the rotating knife edge apertures of the Spectra-Tech microscope, after which the spectrum was recorded. In the equipment used, the resolution was 4 cm^{-1}.

IR-spectroscopy of fibres

Protruding fibres were obtained by tearing the paper samples. These were masked with the two adjustable knife edges before recording the transmission spectra of the fibres.
Reflection spectra were obtained using an area of 3 x 5 mm, this technique will be referred as Mirror reflection.

The effect of sulphur dioxide on paper

To investigate the effect of SO_2 on paper, handsheets were made from the bleached sulphite softwood cellulose. The paper was exposed to 50±5 ppm sulphur dioxide for 8 weeks in a stainless steel cabinet. The conditions during the first four weeks were 20±1°C and 65±2% RH. Samples were taken at the end of this period. During the next four weeks the conditions were 40±2°C and 65±5% RH. Reference samples were stored in a separate cabinet, without SO_2 (Havermans and Versluijs 1988; Havermans 1990). After the exposures all samples were kept in the dark at 23±2°C and 50±5% RH. These samples were subjected to infrared spectroscopy and the pH of the cold water extract and the copper number (ASTM 1971; ASTM 1992) were determined in order to measure the acidity, caused by carboxylic groups formed and deposits of SO_2, and the amount of reducing aldehydes and reactive keto groups after the artificial exposure.

An overview of the techniques used

Since all materials were not used for the same applications, a summary is given in Table 2.3.

Table 2.3 *Matrix of the IR analytical techniques used*

Material	Reflection			Transmission	
	Mirror	DRIFT	ATR	KBr	Microscopy
Cellulose (native)				v	
Cellulose (micro-crystalline)	v			v	
Bleached sulphite softwood Cellulose	v	v	v	v	v
Hardwood lignin (beech)				v	
Softwood lignin (larch)				v	

Before being evaluated, all spectra were base-line corrected by setting the intensities at 4000, 2600, 1900, 840 and 400 cm^{-1} to 0. The presentation of the spectra is therefore comparable with that in the articles by Hon and Hemmingson (Hon 1979; Hon 1984; Hemmingson and Wong 1989). All the spectra in this section are presented as absorbency *vs.* wavenumber.

2.3 Results and discussion

2.3.1 Cellulose and lignin

The recorded infrared spectra of cellulose (native, cotton) and lignin (both softwood and hardwood) are shown in Figures 2.1 and 2.3a and 2.3b respectively. The molecular structures of cellulose and lignin are presented in Figures 2.2 and 2.4a and 2.4b. The interpretation of the spectral bands is given in Tables 2.4 and 2.5. It should be noted that all spectra given in this section are absorbency spectra, and the wavenumber associated with a bond can be read as the peaks in the spectra.

According to Barker *et al.*, a cellulose type I band should be found at 920 cm^{-1}, but this was not the case in our cellulose spectra. However, a bond at 895 cm^{-1} was found, indicating that the β-anomer bond is present. Furthermore, a weak band at 710 cm^{-1} indicated that the native cellulose used can be classified as type I.

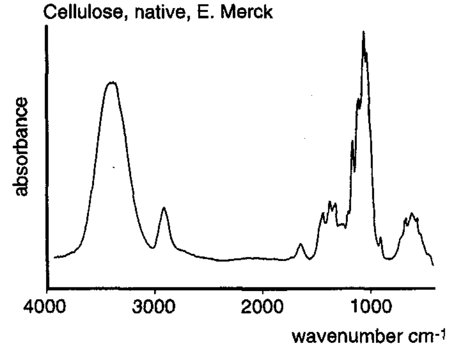

Figure 2.1 *Transmission spectrum of native cellulose (measured in KBr). The wavenumbers are given on the x-axis decreasing from left to right, and the relative absorbance is given on the y-axis. The spectrum was FFT-smoothed with a factor 3 and base line-corrected*

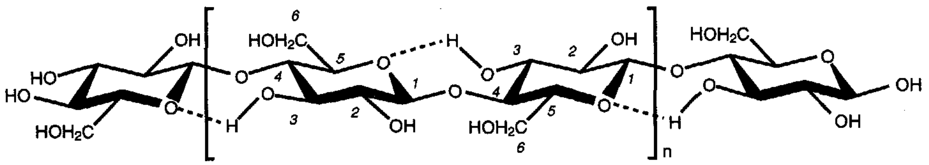

Figure 2.2 *The structural formula of cellulose, a linear homopolysaccharide composed of β-D-glucopyranoside units linked by (1→4) bonds*

Table 2.4 *Peak table and interpretation of the spectrum of native cellulose. The intensity (i) is given at four levels: s = strong, m = medium, w = weak, b = broad*

Wavenumber cm^{-1}	I	Interpretation *
3355	b	O-H stretching vibration R-OH, broad band 3770-3000 cm^{-1}
2900	s	C-H stretching vibration (CH, CH_2), broad band 2990-2790 cm^{-1}
1640	m	O-H stretching vibration, water in cellulose
1430	m	CH_2 bending vibration, internal deformation (scissoring)
1370	m	C-O-H bending vibration
1320	m	CH_2 bending vibration, external deformation (wagging)
1200	s	C-O-H bending vibration
1160	s	C-O stretching vibration (C_1-O-C_5)
1110	s	C-O-C symmetrical stretching vibration
1060	s	C-O-C asymmetrical stretching vibration
1035	s	O-H bending vibration (primary alcohol)
895	m	skeletal vibration -anomer cellulose
710	m	CH_2 rocking, cellulose type I
665	m	C-OH bending vibration, out of plane (bound)

* references (Bellamy 1959; Higgins, Stewart *et al.* 1961; Zhbankov 1966; Durig, Esterle *et al.* 1988; Kuo, McClelland *et al.* 1988)

The typical lignin bands in the infrared spectrum are at approximately 1510 cm^{-1} and 1600 cm^{-1} (aromatic ring vibrations) and between 1460 and 1470 cm^{-1} (C-H deformation vibrations and aromatic ring vibrations) as can be seen in Figures 2.3a and 2.3b. The interpretation of these spectra is given in table 2.5. The ratio between the intensities of the bands at 1510 and 1600 cm^{-1} is often used to distinguish between softwood and hardwood lignin (Fengel and Wegener 1989). We found that in the hardwood lignin the intensities of these two bands are almost the same. This is in agreement with the literature. Fengel and Wegener (1989) attributed this to the unconjugated *syringyl* units present in *hardwood lignin.* For the softwood lignin, we found that the intensity of the band at 1510 cm^{-1} (ascribed to unconjugated *guaiacyl* compounds in *softwood lignin*) was much higher than the intensity of the band at 1600 cm^{-1}, which is also in agreement with statements given in the literature, for example Fengel and Wegener (1989).

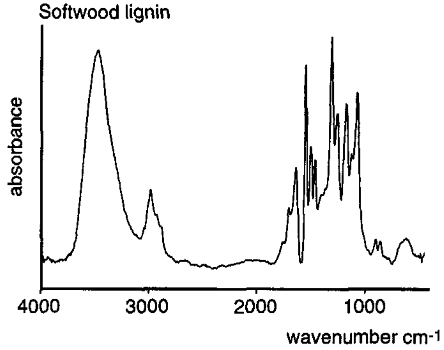

Figure 2.3a Transmission spectrum of softwood (Larch) lignin (measured in KBr). The wavenumbers are given on the x-axis decreasing from left to right, while the relative absorbance is given on the y-axis. The spectrum was FFT-smoothed with factor 3 and base line-corrected

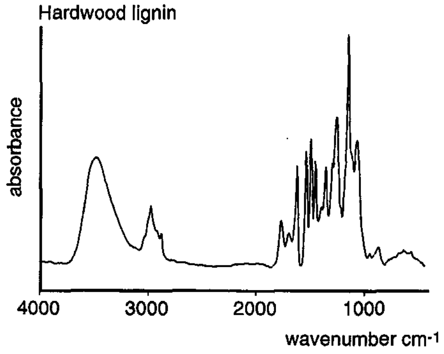

Figure 2.3b Transmission spectrum of hardwood (Beech) lignin (measured in KBr). The wavenumbers are given on the x-axis decreasing from left to right, while the relative absorbance is given on the y-axis. The spectrum was FFT-smoothed with factor 3 and base line-corrected

Table 2.5 *Peak table and interpretation of the IR transmission spectra of lignin*

Wavenumber cm^{-1}		Interpretation *
Beech	**Larch**	
3455	3445	OH stretching vibration
2995	2995	CH stretching vibration (CH aromatics)
2940	2940	CH stretching vibration (CH_2)
2845	2845	CH stretching vibration (CH_3)
1740	1725	C=O stretching vibration (not aromatic conjugated)
1665	1665	C=O stretching vibration (aromatic conjugated), the 1640 H-O-H stretching vibration overlaps this band
1595	1600	C=C aromatic skeleton vibration
1505	1510	C=C aromatic skeleton vibration
1460	1465	CH_2 asymmetrical bending vibration
1420	1420	C=C aromatic skeleton vibration
1365	1360	CH_3 symmetric bending vibration
1330	1325	aromatic ring vibration (syringyl unit)
1265	1270	aromatic ring vibration (guaiacyl unit)
1225	1220	aromatic ring vibration (syringyl unit)
1125	1140	CH bending vibration, aromatic
absent	1085	CH bending vibration, aromatic
1035	1035	lignin skeleton vibration
absent	860	1,3,4 substitution pattern, aromatic (guaiacyl unit)
835	absent	1,3,4,5 substitution pattern, aromatic (syringyl unit)
absent	820	1,3,4 substitution pattern, aromatic (guaiacyl unit)

* references (Bellamy 1959; Saad, Issa *et al.* 1980; Schultz, Templeton *et al.* 1985; Fengel and Wegener 1989)

The bands at 860 and 820 cm^{-1} are generally associated with softwood lignin, while the band at 835 cm^{-1} is associated with hardwood lignin (Bellamy 1959; Saad, Issa *et al.* 1980; Fengel and Wegener 1989). However, Figures 2.4a and 2.4b show that the 1,3,4- and the 1,3,4,5-substitution pattern may occur in both softwood and hardwood lignin.

The model used for the softwood lignin is according to Adler, and comprises 16 prominent C_9-units, derived from the results of oxidative degradation experiments on spruce lignin. The appearance of one syringyl unit (No. 13), for example, is not quantitative, and the pinoresinol unit (Nos. 10,11) probably overemphasises this structural element (Adler 1977). One of the models for hardwood lignin was obtained in a similar way, and Nimz calculated the proportions of 10 types of linkages between the C_9-units in beech lignin and proposed a structural formula (Nimz 1974).

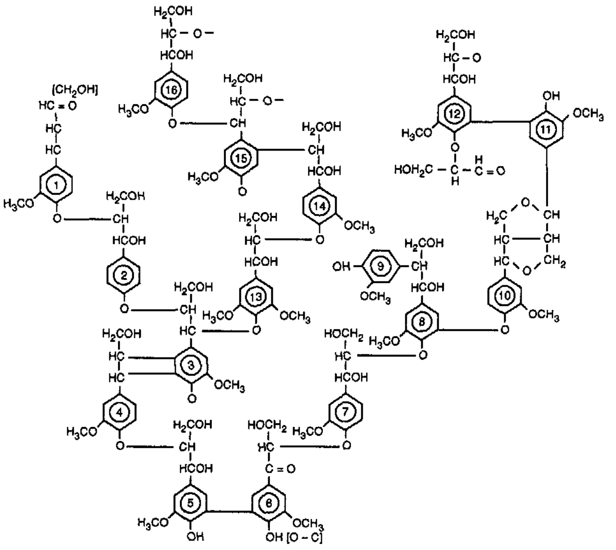

Figure 2.4a *Representation of the structural formula of a softwood lignin according to Adler (1977), a polymer made mainly of phenyl propane units. Softwood lignin consists mostly of guaiacyl units*

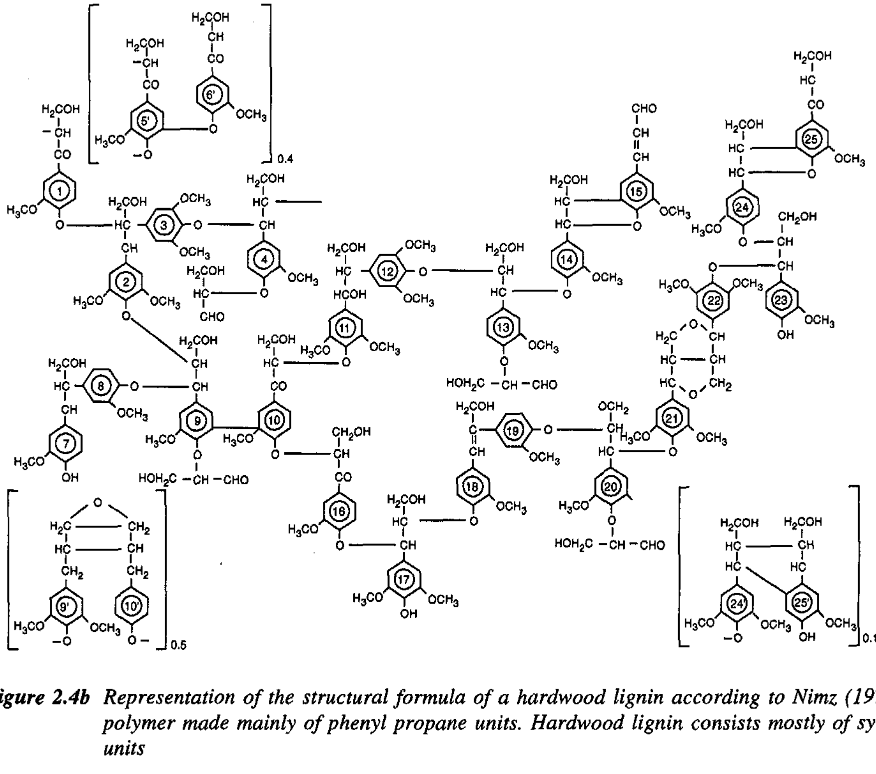

Figure 2.4b *Representation of the structural formula of a hardwood lignin according to Nimz (1974), a polymer made mainly of phenyl propane units. Hardwood lignin consists mostly of syringyl units*

2.3.2 Different types of cellulose

Although all the materials are classified as cellulose, differences in composition were found using infrared spectroscopy. The spectra of the four cellulose samples, the native, the Avicel, the microcrystalline and the bleached softwood cellulose, show characteristic differences, as can be seen in Figure 2.5. The peak tables are listed in Table 5.

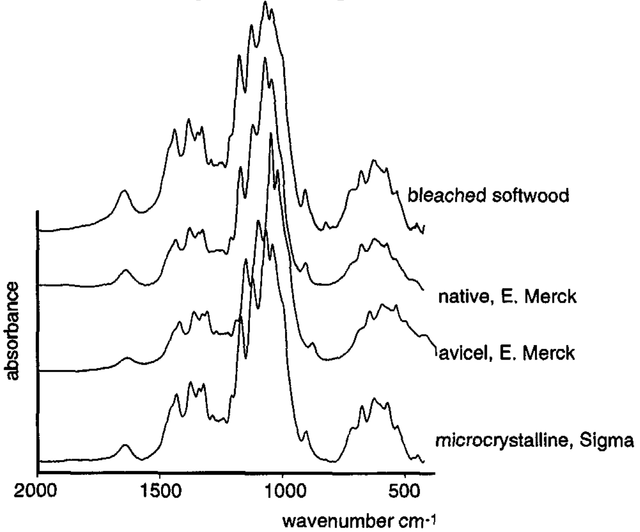

Figure 2.5 *Transmission spectra of four cellulose samples (measured in KBr). The wavenumbers are given on the x-axis decreasing from left to right, while the relative absorbance is given on the y-axis. The spectra were FFT-smoothed with factor 3 and base line-corrected*

Table 2.5 *Peak table of the bands of the various cellulose samples. The wavenumbers are expressed in* cm^{-1}

bleached softwood	native	Avicel	microcrystalline
1375	1370	1370	1370
1320	1320	1320	1320
1200	1200	1200	1200
1165	1160	1160	1165
1115	1110	1110	1110
1060	1060	1060	1060
1035	1035	1035	1030
990	990	990	990
895	895	895	895
815	absent	815	815
705	710	710	705
670	665	670	665
620	615	absent	615
560	560	560	560
520	525	525	525
absent	440	absent	absent

It can be seen, that all the cellulose samples do indeed contain the β-anomeric bond (895 cm^{-1}) and, because a band is present at 710 cm^{-1}, it can be concluded that the celluloses are of type I (Barker, Bourne *et al.* 1954; Zhbankov 1966; Sugiyama, Vuong *et al.* 1991).

Three significant differences can be observed.

1) The differences in peak sharpness and peak width in the 1600 - 900 cm^{-1} range can be explained by the possible crystalline forms of cellulose samples (Nelson and O'Connor 1964; Zhbankov 1966). Nelson and O'Connor stated that "... as cellulose may be present in various polymorphic states, these polymorphic states will be associated with a defined number of degrees of freedom of the possible vibrations of cellulose. As the crystallinity increases, these degrees of freedom will decrease, thus resulting in a more clearly defined pattern of bands".
2) The spectrum of native cellulose shows an additional band at approximately 440 cm^{-1}. According to Zhbankov, this band is specific for cotton cellulose.
3) Three out of four cellulose spectra show an *additional band* at 815 cm^{-1} (see Figure 2.6a). This is particularly apparent in the paper spectrum. It is clearly weaker in the microcrystalline and Avicel cellulose spectra. This band is not evident in the native cellulose spectrum for which the raw material was cotton.

Micrograph were also made from the cellulose samples using Scanning Electron Microscopy, SEM (see Figure 2.6b). These micrographs show, that the fibre structures of the Avicel, the microcrystalline and the bleached softwood cellulose are somewhat comparable and that the fibres were obtained from wood cellulose.

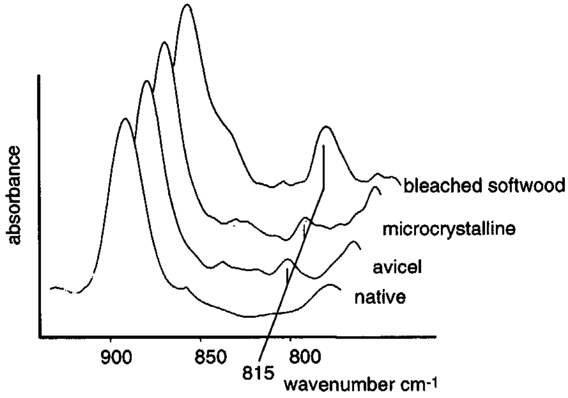

Figure 2.6a *Transmission spectra of cellulose samples (measured in KBr). The wavenumbers are given on the x-axis decreasing from left to right, while the relative absorbance is given on the y-axis. The spectra were FFT-smoothed with factor 3 and base line-corrected. A band occurs at 815 cm^{-1} for the softwood cellulose and both commercial cellulose types: the microcrystalline from Sigma and Avicel from Merck. Note that the 815 cm^{-1} band is absent in the native cellulose spectrum*

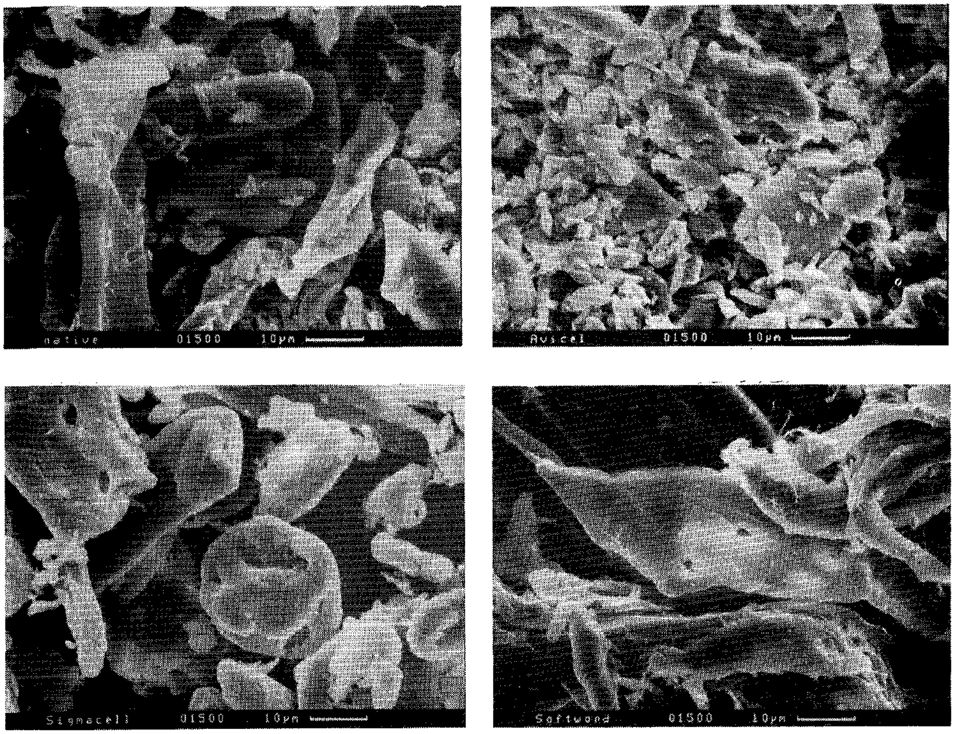

Figure 2.6b *Scanning Electron Micrographs of four cellulose samples (magnification is 1500 times). From left to right and from top to down: native cellulose, Avicel cellulose, microcrystalline cellulose, bleached sulphite softwood*

The band at 815 cm^{-1} may be due to skeletal vibrations of *e.g.* $C(CH_3)_2$ or $C(CH_2)(CH_2)C$ type groups (Bellamy 1959). Owen and Thomas (1989) report spectra of holocellulose, which is a mixture of cellulose and hemicellulose. Although these authors did not discuss the significance of the spectra in detail, the reader may observe a typical band at approximately 815 cm^{-1} (Owen and Thomas 1989). Given this information we decided to extract the softwood paper to separate the hemicellulose from the cellulose. Procedures to isolate hemicellulose are given by Browning (1967) and Fengel and Wegener (1989). Pieces of paper were stirred for four hours in 10% aqueous NaOH to obtain a pulp and to dissolve the hemicellulose. The filtered colloidal solution was then acidified with acetic acid (pH = 6) and subsequently mixed with excess alcohol (96%). After being allowed to settle, the precipitated hemicellulose was collected by filtration. After drying for 24 hours at 103°C, its transmission spectrum was recorded. The spectra of the original softwood cellulose and of the extract, the hemicellulose, are shown in Figure 2.7.

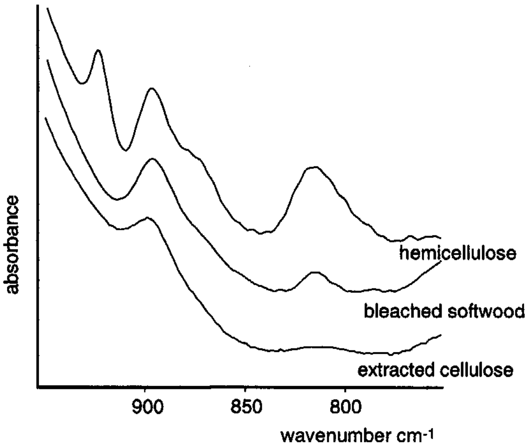

Figure 2.7 *Transmission spectra (KBr) of the extracted softwood hemicellulose and of the original softwood cellulose. The wavenumbers are given on the x-axis decreasing from left to right, while the relative absorbance is given on the y-axis. The spectrum was FFT-smoothed with factor 3 and base line-corrected. The extract shows a peak at 815 cm*$^{-1}$ *similar to that in the raw material. This peak is absent in the extracted cellulose, thus this peak does not belong to cellulose but to hemicellulose*

As can seen in Figure 2.7, the peak at 815 cm^{-1} is clearly visible in both the bleached softwood and the hemicellulose. This band was absent in the extracted softwood cellulose, and therefore with respect to the literature we concluded that this band belongs to skeletal vibrations of hemicellulose (Bellamy 1959; Zhbankov 1966).

Some other peaks in the area under consideration emerge very faintly, if at all, in the spectrum of the bleached sulphite softwood cellulose. For example, the shoulder at approximately 875 cm^{-1} in the cellulose spectrum has become a distinct band in the hemicellulose spectrum. According to Zhbankov (1966), this band, which is also present in the spectra of a xylan and of α-D-xylose is due to the CH_2 (swing) of the CH_2-OH present. Zhbankov (1966), discussed the appearance of the 920 cm^{-1} in the spectra of some sugars. This band occurs in our hemicellulose spectrum. Firstly, this band could be a C-O stretching vibration of an ethyl ether that has been formed due to the drying of the extract in an oven after washing with ethanol. Secondly, some free α-D-glucose might be present.

2.3.3 Cellulose crystallinity

There is a difference in the spectra which cannot be directly observed, and which may be related to the degree of crystallinity of the different types of cellulose. The bands in the cellulose spectra at 1372 cm^{-1} and 2900 cm^{-1} represent the CH_2 bending vibration and the CH_2 stretching vibrations, respectively. The ratios of the intensities of these peaks is of significance (Nelson and O'Connor 1964; Nelson and O'Connor 1964; Fengel and Wegener 1989) and is called the crystallinity index (CI). In our study, the base-line of the cellulose spectra was corrected before determining the intensities. The base-line of the band at 1372 cm^{-1} was set to zero at 1400 and 1350 cm^{-1} and that of the band at 2900 cm^{-1} was set to zero at 3000 and 2750 cm^{-1}. Table 2.6 lists the averages of four measurements made for each type of cellulose.

Table 2.6 *Mean ratios of the peak intensities at 1372 cm^{-1} and 2900 cm^{-1} representing the crystallinity index (CI)*

Cellulose type	**CI**	**Standard deviation**
Microcrystalline	0.44	0.02
Native	0.401	0.001
Bleached sulphite softwood	0.402	0.002
Avicel	0.646	0.002

The results show that the Avicel cellulose material has by far the highest CI. According to Nelson and O'Connor (1964), the higher the CI the higher is the degree of crystallinity. So, it can be concluded that Avicel has the highest degree of crystallinity, followed by microcrystalline cellulose. Bleached sulphite softwood and Native cellulose were comparable and have the lowest score. This order of crystallinity is confirmed by the spectra of deuterated bleached sulphite softwood and deuterated microcrystalline cellulose. As described by Marrinan and Mann (1954 and 1955), the ratio of the OD band intensity to the OH band intensity provides a measure of the amorphous fraction (Marrinan and Mann 1954; Marrinan and Mann 1956) since the amorphous parts are accessible to water and D_2O.

After either 4 or 24 hours of exposure to D_2O vapour at 23°C, the spectrum of deuterated bleached sulphite softwood indicated an effective exchange of the water. After 4 hours exposure, the infrared spectrum remained stable, indicating that a 4 hour exposure is indeed sufficient to reach equilibrium. The incorporation of the D_2O vapour by the bleached sulphite softwood is indicated by the appearance of a band at approximately 2515 cm^{-1} (vOD) while the band at 1640 cm^{-1} (vOH, bound water) disappeared (Figure 2.8) and a weak band appeared at 1235 cm^{-1}. Thus the band at 1640 cm^{-1} is associated with bound water.

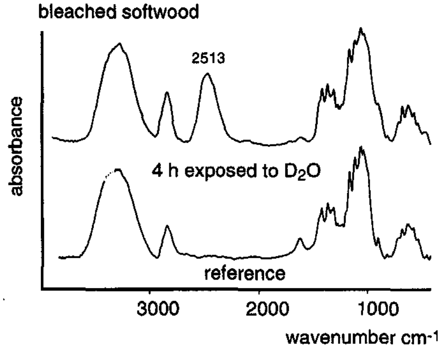

Figure 2.8 *Transmission spectra (KBr) of the deuterated (D_2O, 23 °C) and normal softwood cellulose. The wavenumbers are given on the x-axis decreasing from left to right, while the relative absorbance is given on the y-axis. The spectra were FFT-smoothed with factor 3 and base line-corrected*

From the spectra obtained, the proportions of OD and OH were calculated on the basis of the areas of the bands at 2300 - 2500 cm^{-1} and 3000 - 3800 cm^{-1}. The results indicate that the microcrystalline cellulose is indeed more crystalline than the softwood cellulose, which is in agreement with the CI-data.

For the bleached sulphite softwood, the calculated OD fraction was approximately 25% (*i.e.* the OH fraction = 75%), and for the microcrystalline cellulose, the calculated OD fraction was approximately 10% (*i.e.* the OH fraction = 90%).

2.3.4 Internal and surface information

By comparing the results of several IR-techniques, the internal and surface structure of cellulose can be discussed.

The reflectance spectra for the bleached sulphite softwood clearly show a distinction from DRIFT (essentially a combination of transmission and reflection) and the reflection spectroscopy of a selected area using IR microscopy (see Figure 2.9). Note that on the y-axis, the data are given in Kubelka-Munk units derived from the Kubelka-Munk function (Software 1990):

$$\frac{(1-(S/R))^2}{2\cdot S/R}=\frac{k}{s} \qquad (1)$$

Here S is the reflectance of the sample, R the reflectance of the reference. For DRIFT, pure KBr was used as reference, while for IR-microscopy a gold plate was used. The calculated values represent the ratio of k, the absorption coefficient, and s, the scattering factor, both depending on the particle size and refractive index of the sample being investigated. The Kubelka-Munk units are linear to concentration, and therefore comparable to the according absorbance spectrum.

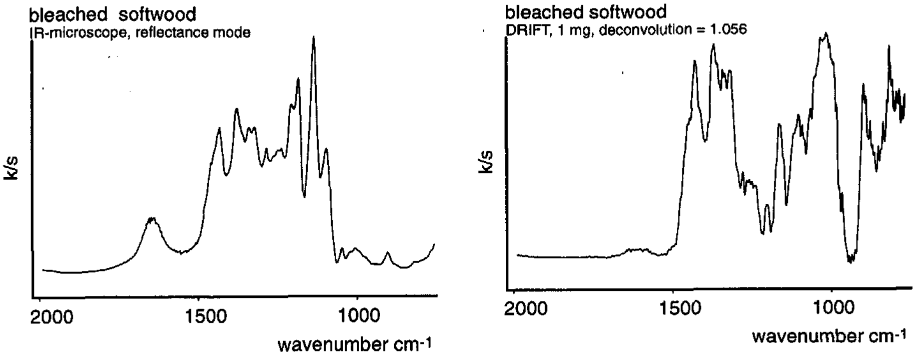

Figure 2.9 *IR reflectance spectra of bleached sulphite softwood. Left: fibres analysed using IR-microscope reflectance spectroscopy, and right: 1 mg of fibres mixed with KBr and measured using diffuse reflectance. The x-axis represents the wavenumbers, while the calculated Kubelka-Munk units are given on the y-axis.*

ATR gave no reproducible spectra, which was also observed by other workers. The reason for this is that the ATR spectrum depends, in part, on the force with which the paper is pressed against the reflectance crystals.

When the Kubelka-Munk-converted DRIFT spectrum is compared with that of the reflectance spectrum obtained with the IR-microscope, it is evident that the C-H and O-H peaks are more clearly shown in the range of 900 - 600 cm^{-1} (Figures 2.9 and 2.10). The hemicellulose peak is clearly visible at 815 cm^{-1}. The water band at 1640 cm^{-1} is least apparent in the DRIFT spectrum. This may be because the water is bound to and situated around the cellulose fibres. According to Kim (1990), the extent of adsorption of water to the surface of paper is less than that to or in the fibres. Comparison of the reflection and transmission spectra shows differences in the region from 1500 to 750 cm^{-1}. The shoulder at 995 cm^{-1} occurs in the transmission spectra of fibres. The intensities of the bands at

1035 cm^{-1} (OH bending vibrations) and 1065 cm^{-1} (C-O-C bending vibrations) related to the band at 1370 cm^{-1} have been reduced (see Figure 2.10).

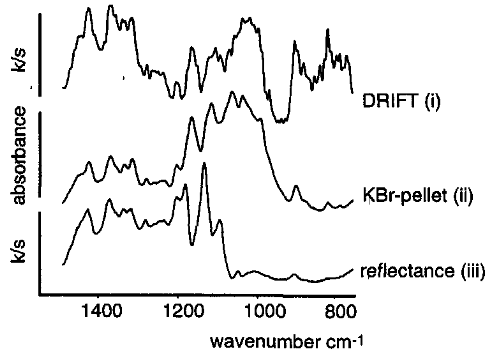

Figure 2.10 *Spectra of bleached sulphite softwood cellulose obtained using three techniques. i: combination of transmission and reflection (DRIFT). ii: transmission spectrum in KBr-pellet and iii: reflectance spectroscopy of a selected area using the IR-microscope*

The three spectra shown in Figure 2.10, provide a rough indication of the functional groups present on the surface of the fibres and inside the fibres. The peak at 815 cm^{-1} indicates the presence of hemicellulose in the fibres. Sulphite pulping of cellulose results in fibres that contain hemicellulose internally (Fengel and Wegener 1989).

The OH-group of the primary alcohol ($R-CH_2-OH$) is most apparent at the surface (1135 cm^{-1}). This corresponds with the structure to cellulose fibres. The anomeric C-O-C bond (987 and 1065 cm^{-1}) occurs clearly in all the spectra. This indicates that this bond occurs both in the fibres and at the surface.

2.4 The influence of SO_2

The cellulose paper was subjected to 50 ppm SO_2 for 8 days at 20°C and 65% relative humidity. The effects of SO_2 have been studied by chemical analyses and by IR spectroscopy.

The pH measurements on the cold-water extracts show an increase in the acidity after the two exposure periods, as can be seen in Figure 2.11. The data for samples exposed without SO_2 show that some acidification occurred after 4 weeks at 20°C and after an increase in temperature, 40°C. In the presence of SO_2, 50 ppm, at 20°C and 65% RH, there is an acidification by the uptake of SO_2. This effect became more pronounced when the exposure was continued at 40°C and 65% RH.

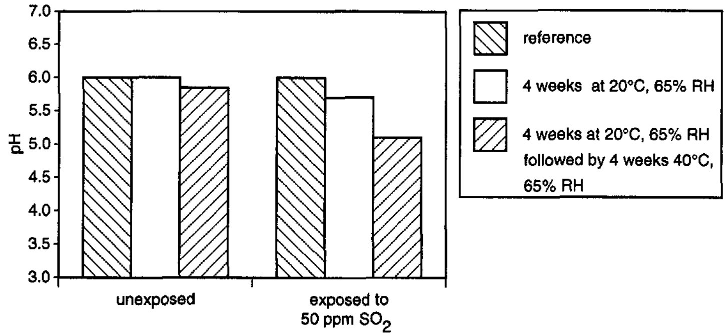

Figure 2.11 *The effects of 50 ppm SO_2 and temperature on the acidity of the bleached sulphite softwood cellulose at 65% RH. The reference materials were exposed in the absence of SO_2*

The pH decreased by 0.2 units in the absence of SO_2 and by 0.9 units for the papers exposed to SO_2.

The copper number data showed a similar pattern (Figure 12).

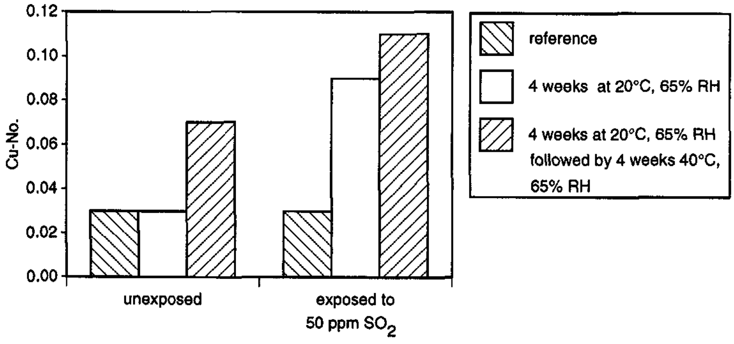

Figure 2.12 *The effect of 50 ppm SO_2 and temperature on the copper number of the bleached sulphite softwood cellulose using 65% RH. The reference materials were exposed to the climate in the absence of SO_2*

Figure 2.12 shows that exposure for 4 weeks at 20°C and 65% RH does not affect the cellulose, whereas the increase in temperature to 40°C gave an increase in the amount of reactive aldehyde and/or keto groups. In the presence of SO_2, the copper number also increased at the lower temperature indicating a greater deterioration. It was shown that in presence of SO_2 the Cu-No. was increased by a factor of 1.6.

IR transmission spectra of the cellulose-based paper before and after exposure to the sulphur dioxide, are given in Figure 2.13.

The spectra clearly indicate that it is difficult to observe changes in chemical properties using infrared spectroscopy. No increases in carbonyl or carboxyl groups were observed, in contrast to the results of the wet chemical analyses indicating an increase in the acidity and copper number of the material exposed to the SO_2. We suggest that this increase is due to the deposition of SO_2 gas on the paper followed by an acid catalysed hydrolysis of the cellulose.

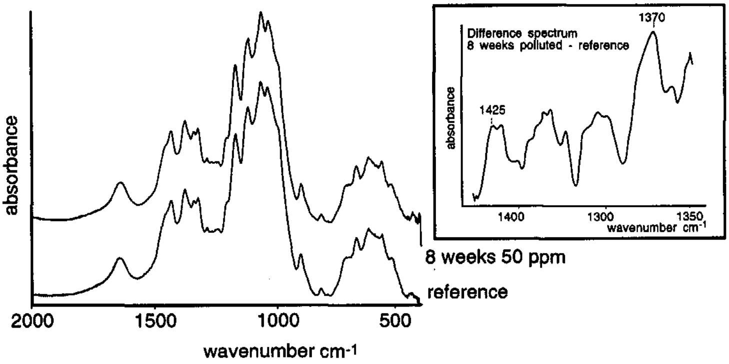

Figure 2.13 Transmission spectra of the bleached softwood cellulose before and after exposure to 50 ppm SO_2 (4 weeks at 20°C + 4 weeks at 40°C and 50% RH). The wave numbers are given on the x-axis decreasing from left to right, while the relative absorbance is given on the y-axis. The spectra were FFT-smoothed with factor 3 and base line-corrected. The outline shows the difference spectrum between the exposed and refference sample

It may be noted that the paper exposed to SO_2 exhibited an increase in crystallinity. The ratio of the intensities of the peaks at 1372 cm^{-1} and 2900 cm^{-1} for the unexposed cellulose-based paper was 0.402 ± 0.002, and for the paper exposed to SO_2 it was 0.44 ± 0.02. This corresponds with the theoretical model (Feller, Lee *et al.* 1986; Young and Rowell 1986; Fengel and Wegener 1989; Iversen and Kolar 1991). According to the authors, in a moderately acid environment, the ordering of the cellulose will increase before the acid-catalysed hydrolysis occurs, and this increases the crystallinity. Figure 2.14 illustrates a model of the increase in crystallinity of cellulose fibres due to the effects of an acid.

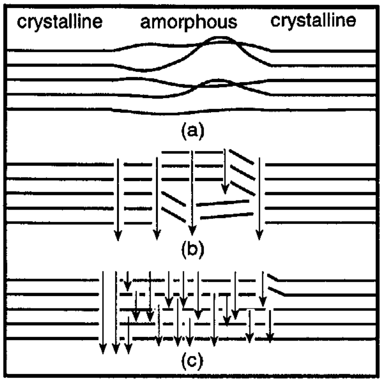

Figure 2.14 A model of the increase in crystallinity due to the effects of an acid according to Young (1986)

From both reflectance and transmission spectra, a remarkable difference was found between the spectra for the exposed and unexposed materials. The intensities of the peaks at 1425 cm^{-1} and 1365 cm^{-1} ($-CH_2$ and C-O-H bending vibrations) were identical in the material exposed to the SO_2, whereas in the spectrum of the original material, the intensity of the 1425 cm^{-1} peak was lower than that of the 1365 cm^{-1} peak. This indicates that there was a decrease in the proportion of alcohol groups on the surface of the cellulose fibrils after the exposure. Due to reordering of the cellulose by the absorption of the SO_2, the acidity increases and therefore the texture will be changed in such a way that the degree of freedom of the C-O-H groups will be reduced. A higher proportion of crystalline regions will occur.

The presence of SO_2 seems to increase the crystalline fraction at 20°C and 65% RH, whereas deterioration of the cellulose occurs when the cellulose is exposed at higher temperatures. The change in the amount of reactive aldehyde and/or keto groups could not be observed using IR, in contrast to the chemical information provided by the copper number. This also indicates the different behaviour of cellulose in a water-based environment. Upon exposure to SO_2 in the presence of moisture, the cellulose can be partially hydrolysed with the formation of so-called hydrocellulose (Rutherford and Harris 1943). During the examination of the copper number, a boiling solution is used, and therefore a fraction of the hydrocelluloses obtained may dissolve. This fraction has a higher reducing power than the original hydrocelluloses when they are investigated in the solid state using FTIR.

2.5 Conclusions

From transmission spectroscopy, it was found that using KBr discs, a high reproducibility was obtained (1 mg sample in 300 mg KBr). This allows the use of a small amount of a sample, which is an advantage, due to the extremely high molecular absorption coefficients of cellulose and of the functional groups in cellulose. The reproducibility using transmission spectroscopy using the IR-microscope depends on the fibre sample. Each fibre may contain contaminations that become visible at the microscopic level. However, together with the other techniques, the microscope technique provides an important contribution to the characterisation of fibrous materials.

It may be stated that infrared spectroscopy makes an important contribution to the characterisation of paper.

- The crystallinity of cellulose is one of its important characteristics. Besides crystalline cellulose domains, amorphous cellulose will generally also be present. Cellulose may be classified by its degree of crystallinity. Two methods are available:
    1. Exchanging water (HOH) by deuterium oxide (DOD). The relationship between peak areas of the OD stretching vibration at 2500 cm^{-1} and the OH stretching vibration at 3400 cm^{-1} is a measure for the amorphous fraction in the cellulose.
    2. The ratio of the intensities of the peaks at 1372 cm^{-1} and 2900 cm^{-1} in the absorbance IR spectrum will result in the crystallinity index (CI).
- Hemicellulose can be detected by its band at approximately 815 cm^{-1}. The presence of this band also indicates that the cellulose was derived from wood.

Paper deterioration

It may be concluded that SO_2 increases the crystallinity of cellulose at 65% RH. The use of the CI can therefore be a test on following the paper acidification by its change in texture. Although an increase in temperature leads to more reactive aldehyde and/or keto groups as measured by the copper number, this was not revealed in the spectra. It is therefore suggested that cellulose exposed to SO_2 will form by partial hydrolysis hydrocellulose, which has a higher reducing power in a (boiled) solution than in its solid state.

Acknowledgement

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References

Adler, E. (1977).
Lignin chemistry. Past, present and future.
Wood Science & Technology 11: 169.

ASTM (1971).
ASTM D 778 ; Hydrogen ion concentration (pH) of buffered paper extracts.

ASTM (1992).
ASTM D 919 ; Copper number of paper and paperboard.

Atalla, R.H. and D.L. VanderHart (1984).
Native cellulose: a composite of two distinct crystalline forms.
Science 223: 283.

Banik, G. and J. Ponahlo (1983).
IRS-untersuch der degradierenden Wirkung von Licht und SO2 auf Pigmentiertes Papier.
Mikrochimica Acta [Wien] 1: 87.

Barker, S.A., E.J. Bourne, M. Stacey and D.H. Whiffen (1953).
Infra-red Absorption Spectra of Dextran and Other Polyglucosans.
Chemistry and Industry : 196.

Barker, S.A., E.J. Bourne, M. Stacey and D.H. Whiffen (1954).
Infra-red Spectra of Carbohydrates. Part 1. Some derivates of D-Glucopyranose.
Journal of the Chemical Society: 171.

Bellamy, L.J. (1959).
The Infra-Red Spectra of Complex Molecules. London, Methuen & Co LTD.

Bouchard, J., G. Garnier, P. Vidal, E. Chornet and R.P. Overend (1990).
Characterisation of Depolymerized Cellulosic Residues Part 2: Residues derived from ethylene glycol solvolyses of cellulose.
Wood Science & Technology 24: 159.

Brown, L., P. Holliday and I.F. Trotter (1951).
The absorption spectra of some cellulose derivates in the 3-f region.
Journal of the Chemical Society 45: 1532–1539.

Durig, D.T., J.S. Esterle, T.J. Dickson and J.R. Durig (1988).
An Investigation of the Chemical Variability of Woody Peat by FT-IR Spectroscopy.
Applied Spectroscopy 42: 1239.

Faix, O. (1988).
Practical Uses of FTIR Spectroscopy in Wood Science and Technology.
Microchimica Acta [Wien] 1: 21.

Faix, O., R. Patt and O. Beinhof (1987).
Grundlagen und Anwendung von FTIR-Spectroscopie bei der Herstellung und Analyse von Zellstoffen.
Das Papier 41: 657.

Feller, R.L., S.B. Lee and J. Bogaard (1986).
The kinetics of cellulose deterioration.
Historic Textile and Paper Materials. Conservation and Characterization.
Washington D.C., American Chemical Society. 329.

Fengel, D. and G. Wegener (1989).
WOOD, Chemistry, Ultrastructure and Reactions. Berlin, Walter de Gruyter.

Fink, H.P. and B. Phillip (1985).
Models of Cellulose Physical Structure from the Viewpoint of the Cellulose I → II Transition.
Journal of Applied Polymer Science 30: 3779.

Gibson, D.G., R.L. Krahmer and R.C. DeGroot (1985).
Early detection of brown rot decay in douglas-fir and southern yellow pine by infrared spectrophotometry.
Wood & Fiber Science 17: 522.

Havermans, J.B.G.A. (1990).
ACBAM Phase 5.1: Investigations on the accelerated ageing of paper under influence of sulfur dioxide.
PK 90.1003, TNO, Delft, The Netherlands.

Havermans, J.B.G.A.; J.P. van Deventer; R. van Dongen; F. Flieder; F. Daniel; P. Kolseth; T. Iversen; H. Lennholm; O. Lindqvist; A.S. Johansson (1994).
The Effects of Air Pollutants on the Accelerated Ageing of Cellulose Containing Materials - Paper.
EC/DGXII/STEP project CT-90-0100, BU3.94/1068/JH.
TNO, Delft, The Netherlands.

Havermans, J.B.G.A. and R.P. Versluijs (1988).
ACBAM Phase 2: The set up of an experimental pollution equipment. HI 88.1179.
TNO, Delft, The Netherlands.

Hemmingson, J.A. and H. Wong (1989).
Characterization of Photochemically Degradated Newsprint Solubles by 13C NMR and IR Spectroscopy.
Holzforschung 43: 141.

Higgins, H.G., C.M. Stewart and K.J. Harrington (1961).
Infrared Spectra of Cellulose and Related Polysacharides.
Journal of Polymer Science (A: Polymer Chemistry) 51: 59.

Hon, D.N.S. (1979).
Photooxidative Degradation of Cellulose: Reactions of the Cellulosic Free Radicals with Oxygen.
Journal of Polymer Science (A: Polymer Chemistry) 17: 441.

Hon, D.N.S. (1984).
Fourier transform IR Spectroscopy and Electron Spectroscopy for Chemical Analyses. Use in the Study of Paper Documents.
Advances in Chemistry Series, Philadelphia, 212, American Chemical Society.

Iversen, T. and J. Kolar (1991).
Effects of nitrogen dioxide on paper. FoU-projektet för Papperskonservering, Report No. 5.

Kim, Y.S. (1990).
Chemical Characterisitcs of Waterlogged Archaeological Wood.
Holzforschung 44: 169.

Kleinert, T.M. (1969).
Altern und Vergilben von Cellulose.
Holzforschung und Holzverwertung 21: 133.

Kuo, M.L., J.F. McClelland, S. Luo, P.L. Chien, R.D. Walker, and C.Y. Hse (1988).
Applications of infrared photoacoustic spectroscopy for wood samples.
Wood & Fiber Science 20: 132.

Lanting, R.W., E.H.P. Logtenberg, J. Muetgeert, H. Nieboer and H.A. Westra (1985).
Veroudering en Aantasting van Cellulose door Luchtverontreiniging.
R 88/145, TNO, Delft, The Netherlands.

Marrinan, H.J. and J. Mann (1954).
A study by infra-red spectroscopy of hydrogen bonding in cellulose.
Journal of Applied Chemistry 4: 204.

Marrinan, H.J. and J. Mann (1956).
The reaction between cellulose and heavy water. Part 1. A qualitative study by infra-red spectroscopy.
Trans Faraday Society 52: 481.

Marrinan, H.J. and J. Mann (1956).
The reaction between cellulose and heavy water. Part 2. Measurement of absolute accessibility and crystallinity.
Trans Faraday Society 52: 487.

Marrinan, H.J. and J. Mann (1956).
The reaction between cellulose and heavy water. Part 3. A quantitative study by infra-red spectroscopy.
Trans Faraday Society 52: 492.

Marton, J. and H.E. Sparks (1967).
Determination of Lignin in Pulp and Paper by Infrared Multiple Internal Reflectance.
Tappi Journal 50: 363.

Michell, A.J. (1988).
Usefulness of FTIR difference spectroscopy for studying the reactions of wood during pulping.
Cellulose Chemistry and Technology 22: 105.

Michell, A.J., A.J. Watson and H.G. Higgins (1965).
An Infrared Spectroscopic Study of Delignification of Eucalyptus Regnans.
Tappi Journal 48: 520.

Nassar, M.M. and G.D.M. MacKay (1984).
Infrared of Wood.
Wood & Fiber Science 16: 441.

Nelson, M.L. and R.T. O'Connor (1964).
Relation of Certain Infrared Bands to Cellulose Crystallinity and Crystal Lattice Type part II. A New Infrared Ratio for Estimation of Crystallinity in Celulose I and II.
Journal of Applied Polymer Science 8: 1325.

Nelson, M.L. and R.T. O'Connor (1964).
Relation of Certain Infrared Bands to Cellulose Crystallinity and Crystal Lattice Types part I. Spectra of lattice Types I, II, III and of Amorphous Cellulose.
Journal of Applied Polymer Science 8: 1311.

Nimz, H. (1974).
Angewandte Chemie International Edition 13: 313.

Owen, N.L. and D.W. Thomas (1989).
Infrared Studies of Hard and Soft Woods.
Applied Spectroscopy 43: 451.

Rutherford, H.A. and M. Harris (1943).
Hydrocellulose. High Polymers. New York, Interscience Publishers, Inc. 164.

Saad, S.M., R.M. Issa and M.S. Fahmy (1980).
Infrared Spectroscopic Study of Bagassa and Unbleached High-Yield Soda Bagassa Pulps.
Holzforschung 34: 218.

Schultz, T.P., M.C. Templeton and G.D. McGinnis (1985).
Rapid Determination of Lignocellulose by Diffuse Reflectance Fourier Transform Infrared Spectrometry.
Analytical Chemistry 57: 2867.

Sjöström, E. (1993).
Wood Chemistry. Fundamentals and Applications. Boston, Academic Press, INC.

Software (1990).
Spectra Calc. Version 2.1. Galactic Industries Corporation.

Sugiyama, J., J. Persson and H. Chanzy (1991).
Combined Infrared and Electron difraction Study of the Polymorphism of Native Cellulose.
Marcromolecules 24: 2461.

Sugiyama, J., R. Vuong and H. Chanzy (1991).
Electron diffraction study of the two crystalline phases occurring in native cellulose from an algal cell wall.
Macromolecules 24: 4168.

VanderHart, D.L. and R.H. Atalla (1984).
Studies of microstructure in native celluloses using solid state ^{13}C NMR.
Macromolecules 17: 1465.

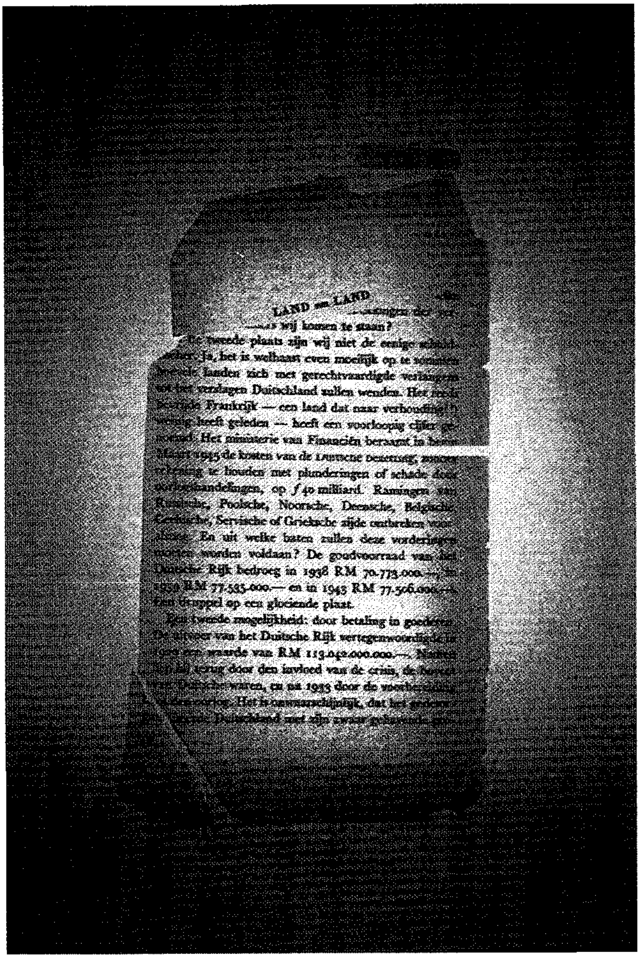
VanderHart, D.L. and R.H. Atalla (1987).
Further evidence for the coexistence of two crystalline forms in native celluloses.
ACS Symposium Series 340(Ch. 5): 88.

Young, A.R. and R.M. Rowell (1986).
Cellulose, Structure, Modification and Hydrolysis. New York, John Wiley & Sons.

Zhbankov, R.G. (1966).
Infrared Spectra of Cellulose and its Derivatives. New York, Consultants Bureau/Plenum Publishing Corporation.

3

Studies on a naturally aged book



LAND [illegible] LAND

[illegible] der [illegible] wij komen te staan?

[illegible] tweede plaats zijn wij niet de eenige schad[illegible]. Ja, het is welhaast even moeilijk op te so[illegible] landen zich met gerechtvaardigde verlangen[illegible] tot het verslagen Duitschland zullen wenden. Het [illegible] Frankrijk — een land dat naar verhouding [illegible] weinig heeft geleden — heeft een voorloopig cijfer genoemd. Het ministerie van Financiën beraamt in [illegible] Maart 1945 de kosten van de Duitsche bezetting, zonder rekening te houden met plunderingen of schade door oorlogshandelingen, op ƒ 40 milliard. Ramingen van Russische, Poolsche, Noorsche, Deensche, Belgische, [illegible], Servische of Grieksche zijde ontbreken vooralsnog. En uit welke baten zullen deze vorderingen moeten worden voldaan? De goudvoorraad van het Duitsche Rijk bedroeg in 1938 RM 70.773.000.—, in 1939 RM 77.535.000.— en in 1943 RM 77.506.000.—. Een druppel op een gloeiende plaat.

Een tweede mogelijkheid: door betaling in goederen. De uitvoer van het Duitsche Rijk vertegenwoordigde in [illegible] een waarde van RM 119.042.000.000.—. Na[illegible] terug door den invloed van de crisis, de [illegible] Duitsche waren, en na 1933 door de voorbereiding [illegible] oorlog. Het is onwaarschijnlijk, dat het [illegible] Duitschland met zijn zwaar gehavende [illegible]

3. STUDIES ON A NATURALLY AGED BOOK

Summary

Naturally aged paper was obtained from the National Library in The Hague and consisted of sheets of paper from the book "Land om Land" by G.B.J. Hilterman, published by NV Uitgeversmaatschappij Elsevier, Amsterdam (1945). The copy used was originally stored at the New York Public Library, USA (1946-1970). Two positions were examined, the so called *margin* and *centre* of the pages, which already showed visually differences. The margin of each page was brown and brittle while the centre was in a better condition. Infrared spectroscopy in KBr was carried out on the paper samples, using a Bruker 113v Fourier Transform Infrared, FTIR, apparatus with a triglycine sulphate, TGS, pyroelectric detector, and a nitrogen-cooled mercury cadmium telluride, MCT, detector operating under vacuum. Spectra were obtained in a range of 4000 - 400 cm^{-1} (25 μm to 2.5 μm) with a resolution of 2 cm^{-1}. Samples were obtained by scraping with a lancet about 1 mg of paper from each page. Chemical analyses have also been performed.

It was concluded, not only visually but also from a chemical and physical viewpoint, that the fibres present in the outer regions (margin) of the sheets differed significantly from the fibres present in the inner regions (centre) of the sheets. The margin fibres were shorter than those of the centre fibres. Scanning Electron Microscopy, SEM, showed that the fibres at the margin were deteriorated more severely than those of the centre of the pages. Thus the cellulose chains had deteriorated. The amounts of acid, reactive aldehyde and keto groups present in the paper from the margin were also higher than those from the centre.

Infrared spectroscopy showed that the crystallinity of the centre of the sheet was much higher than that of the margin and that, the centre of the sheet also contained more ester groups than the margin, probably a lignin-polysaccharide complex.

These results together with the brittleness of the paper, indicate that the ageing processes in the book were caused mainly due to bad storage conditions (*e.g.* high temperature).

3.1 Introduction

The objective of this study was to determine the cause of ageing processes using infrared spectroscopy of paper from a naturally aged book. The study formed a part of The Netherlands Research program on Paper Preservation, better known as the Dutch ACBAM project and was carried out in 1990 (Havermans 1991).

Paper is a complex matrix of materials based on cellulose. Depending on its origin, the matrix may also contain lignin, polysaccharides, fillers (clay or calcium carbonate) and size. Research on paper ageing is based mostly on accelerated ageing tests. By using high temperatures and humidities, the deterioration processes are simulated and accelerated. The performance of the paper is assessed in terms of the changes in chemical, physical and mechanical properties.

Chemical changes can be detected by infrared (*IR*) spectroscopy. IR spectroscopy of cellulose has been used since the 1950's (Brown, Holliday *et al.* 1951), although the direct application of this technique to sheets of paper was introduced only later (Hon 1984). The identification of the ageing processes using IR analysis of paper also requires an appreciation of historical developments in the area of paper-making and in the storage conditions used for the papers, since both the sources of the raw material (cellulose) and the additives have changed over the years. Cellulose, for example, contains several polymorphous structures, all of which affect the IR spectrum. The structure of cellulose can be also changed due to the application of conservation agents.

Several researchers have used IR spectroscopy to study the ageing and yellowing of paper. Kleinert used Fourier Transform Infrared, FTIR, and IR spectroscopy to investigate the photo-oxidative degradation of paper (Kleinert 1969). The reaction mechanism was largely studied in terms of the carboxylic acid groups that were formed. For this purpose, aqueous extracts of the paper were analysed. The photo-oxidation of cellulose generally results in the formation of carboxyl groups, but the author did not observe bands at approximately 1735 cm^{-1} or 1600 cm^{-1}. There was a difference in intensity at 1640 cm^{-1} between the original material and the oxidised product, but the conclusion that photo-oxidation can be monitored using the intensity of the band at 1640 cm^{-1} is dubious. Zhbankov (1966) and others demonstrated earlier that the 1640 cm^{-1} band is due to absorbed water (Zhbankov 1966). Hon also investigated the photo-oxidative decay with UV radiation of paper and concluded that it results in the formation of carbonyl, carboxyl and hydroperoxide groups on the cellulose polymer (Hon 1979; Hon 1984). It was also found that the effects on paper of gases such as SO_2 and NO_2 can be detected by IR or FTIR. In contrast, Banik concluded that exposure of unpigmented paper to SO_2 and light does not result in any significant change in the IR spectrum. However, when paper pigmented with copper compounds was used, changes were observed after exposure to SO_2 and light (Banik and Ponahlo 1983), but this article explains neither the nature of the changes in the IR or FTIR spectrum nor their background.

Hemmingson and Wong (1989) studied the photo-oxidative degradation of newsprint. The paper was exposed to direct and indirect (shade) sunlight. After 8.5 months, the paper was extracted with a water/acetone mixture. The extracted material was analysed with IR and FTIR (liquid between KBr pellets) and NMR. After exposure to direct sunlight carboxylic acid compounds were detected in the aqueous extract, together with lignin and sugar fragments. Sugar fragments were not found after exposure to indirect sunlight. Vanillic acid (4-hydroxy-3-methoxybenzoic acid), resulting from the oxidation of lignin, was one of the dominant monomeric products. Significant differences in the spectra of the extracts were observed in the range from 1100 to 1030 cm^{-1}. The main conclusions were that hemicellulose fragments can be detected in water/acetone extracts and that there was a significant difference in aldehyde group levels.

The ageing of pulps was studied by Forsskåhl and Janson. Unbleached and peroxide-bleached groundwood and chemi-mechanical pulps were subjected to treatment with light followed by heat or by light and heat applied at the same time. By means of diffuse reflectance IR Fourier transform (DRIFT) spectra, it was shown that irradiation increased the intensity of carbonyl and carboxyl groups substantially in the unbleached pulps. Moreover irradiation caused a decrease in the aromatic ring content of the pulps. It was concluded that thermal or light-induced yellowing of pulps represents only a minor part of the total oxidation and degradation processes caused by the physical treatments (Forsskåhl and Janson 1992).

From the literature reviewed, it can be concluded that ageing of paper is generally apparent in the IR spectra as an increase of carboxylic acid and/or carbonyl groups. Ageing will reduce the aromatic ring content in groundwood-containing paper. Furthermore, changes in the morphological structure of cellulose will occur.

3.2 Experimental

The paper studied in this project was obtained from the Dutch National Library in The Hague and consisted of sheets of paper from the book “Land om Land” by G.B.J. Hilterman, published by NV Uitgeversmaatschappij Elsevier, Amsterdam in 1945. The copy used was originally stored at the New York Public Library, USA. Samples of paper from the book were obtained by removing two pages from the book. Previous research indicated that this copy had been exposed to large temperature changes and also that the sulphur dioxide concentration in the storage environment was considerable higher than for an identical copy, which had been stored in The Netherlands (Porck 1988). The storage preriod was from 1946 till 1970. Our investigations focused on the American copy because:

- The American copy was in a worse condition than the copy stored in The Netherlands, especially at the margins of the pages.
- Previous research had shown that paper degradation of a comparable book collection from the New York Public Library is due, in part, to air pollution, because the margins of the American copy appeared to have a higher sulphur content than the Dutch copy (Porck *et al.*, 1988; Porck, 1990).

All pages were in a heavily deteriorated state. After assessing the extent of brown colouration, two locations were defined:

Margin:	Within approximately 0.5 cm of the margin,
Centre:	Approximately 5 cm from the margin.

Spectra were obtained from a single page of this book. The sample was obtained by scraping with a lancet about 1 mg of paper from the page and mixing this sample with about 300 mg KBr (Merck, spectroscopic grade). This mixture was transferred to a die and pressed to a KBr pellet using a pressure of 8 to 10 tonnes for 10 minutes. Transmission spectroscopy in KBr was carried out, using a Bruker 113v FTIR apparatus with a triglycine sulphate, TGS, pyroelectric detector, and a nitrogen-cooled mercury cadmium telluride, MCT, detector operating under vacuum. Spectra were obtained between 4000 and 400 cm^{-1} (25 μm to 2.5 μm) with a resolution of 2 cm^{-1}. All transmission measurements were carried out at least in duplicate. The spectra obtained were base line-corrected by setting the intensities at the points 4000, 2600, 1900, 840 and 400 cm^{-1} to 0. In this way, the presentation of the spectra is comparable with that in the articles by Hon, and Hemmingson and Wong (Hon 1979; Hon 1984; Hemmingson and Wong 1989).
Chemical analyses were performed on the paper and the acidity (pH), copper number and the intrinsic degree of cellulose polymerisation were measured (ASTM 1971; NEN 1981; TAPPI 1985; TAPPI 1988; ASTM 1992).

3.3 Results and discussion

3.3.1 The IR spectra of the book related to its performance

The quality of the margin and the centre of the page are visually different, as can be seen in the pictures in Figure 3.1a-c.

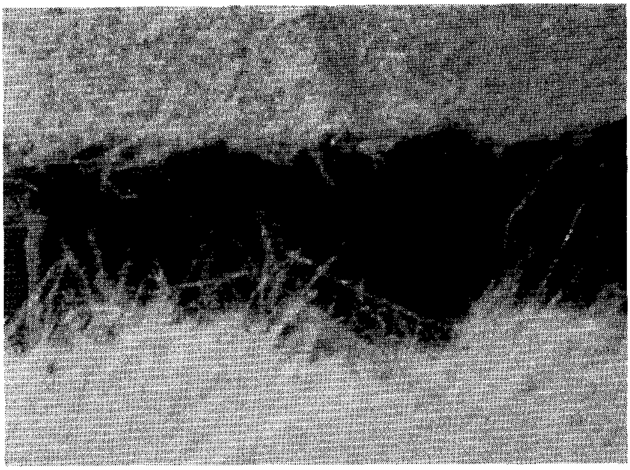


Figure 3.1a *Microphotograph of the fibres, present in the margin (top) and centre (down) of the page from the book "Land om Land", enlarged 200x*

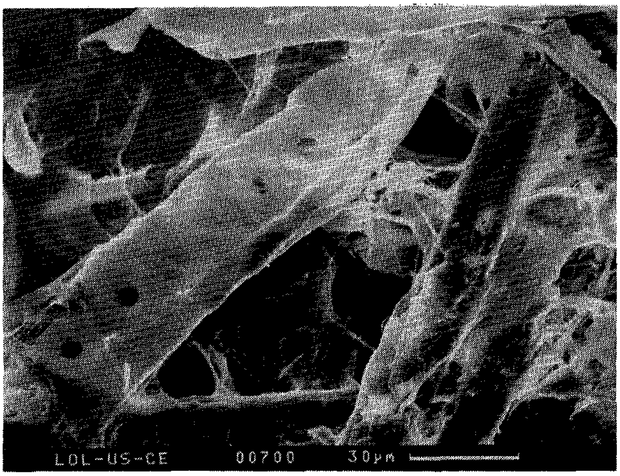


Figure 3.1b *SEM Microphotograph of the fibres, present in the centre of the page from the book "Land om Land", enlarged 700x*

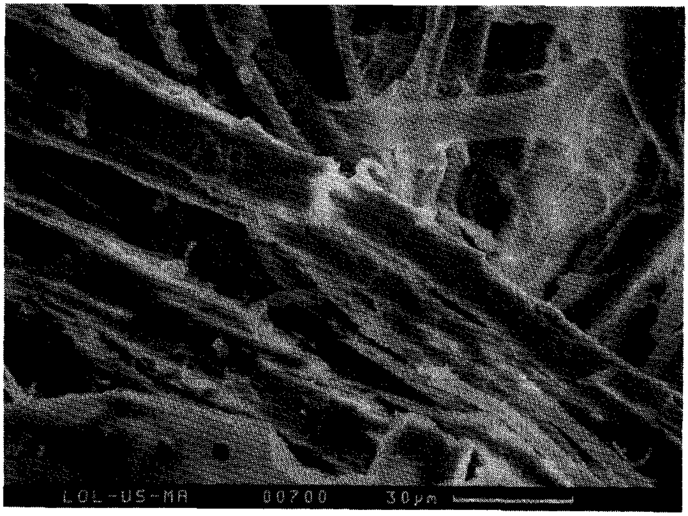


Figure 3.1c *SEM Microphotograph of the fibres, present in the margin of the page from the book "Land om Land", enlarged 700x*

The margin has turned brown while the centre of the page looks still good. From the Figures 3.1a - 1c, it can be seen that the fibres are different: in the centre of the page they are long, whereas at the margin of the page, the fibres are very short and "flat". From the SEM micrographs it becomes apparent that these fibres also showed intrafibrillar cracks.
The corresponding IR transmission (2000 to 400 cm^{-1}) spectra are presented in Figure 3.2. The spectra also show a clear difference between the margin and the centre of the book particularly in the area from 1600 to 1800 cm^{-1} (see Figures 3.2 and 3.3).

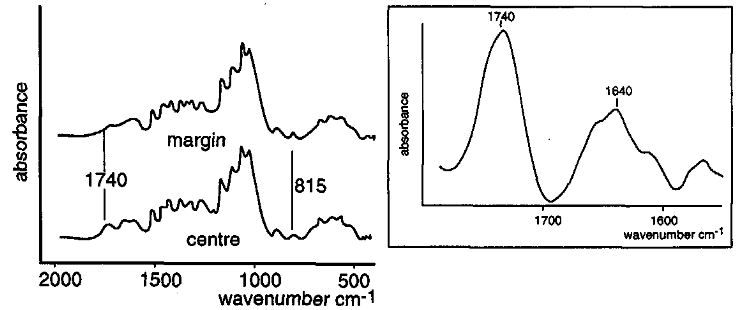


Figure 3.2 *IR spectra of the centre (lower spectrum) and of the margin (upper spectrum) of a page from the book "Land om land".*
Box: The Difference spectrum of the centre and the margin (1500-1800 cm^{-1} region)

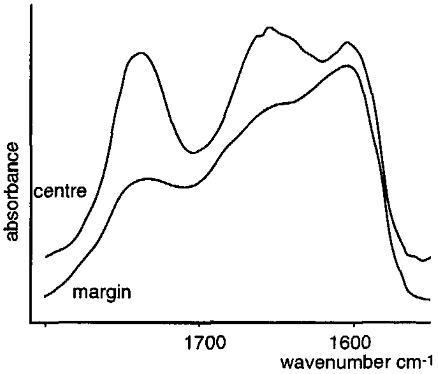


Figure 3.3 *Differences in the area 1600 - 1800 cm^{-1} between the margin and the centre of the book "Land om Land"*

3.3.2 The IR spectra related to the composition of the paper used in the book

The book was printed in 1945. This suggests that the paper may contain groundwood. Visually this can be detected by the presence of brown wood fibres in the paper. The IR spectra showing bands at 1600 cm^{-1}, at 1510 cm^{-1} and at 1460 cm^{-1} indeed indicate the presence of an aromatic compound (C=C conjugated stretching vibrations), which suggests the presence of lignin. The band at 815 cm^{-1} indicates the presence of hemicellulose. Both polymers are found in wood.

Typical lignin bands in the infrared spectrum are found at approximately 1510 cm^{-1}, 1600 cm^{-1} (aromatic ring vibrations) and between 1460 and 1470 cm^{-1} (C-H deformation vibrations and aromatic ring vibrations). The ratio of the intensity of the band at 1510 to that of the band at 1600 cm^{-1} was used to distinguish between softwood and hardwood lignin (Fengel and Wegener 1989). We found that the intensity of the band at 1510 cm^{-1} is considerably higher than that of the intensity of the band at 1600 cm^{-1}. According to statements given in the literature (*e.g.* Fengel and Wegener 1989) this can be ascribed to the unconjugated guaiacyl compounds which are present in softwood lignin.

Figure 3.4 presents the spectrum of the book page (centre) minus the spectrum of native cellulose (Merck, p.a.). The CH_2 stretching vibration band (2900 cm^{-1}) was used for normalisation. In the region from 1900 to 900 cm^{-1} the difference spectrum was compared with the spectrum of softwood lignin. This confirmed the presence of softwood lignin too. It can therefore be concluded that the paper of the book "Land om Land" was made with softwood groundwood. An analysis of the fibre composition also showed that the material is almost 100% softwood groundwood (Fuit 1990).

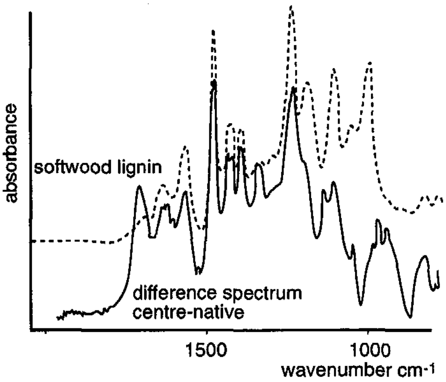


Figure 3.4 *Difference spectrum obtained from the spectrum of the fibres from the book minus the spectrum of native cellulose (lower spectrum) compared to the spectrum of softwood lignin (upper spectrum)*

3.3.3 Differences between the fibres taken from margin and the centre location

Some chemical properties of the margin and centre parts of the page are given in Table 3.1.

Table 3.1 *pH and copper number of the margin and centre parts*

Origin	pH	Cu-No.
Margin	4.3	5.4
Centre	5.5	3.8

From Table 3.1, it can be seen that the pH of the water extract (TAPPI 1988) from pieces of the paper taken from the margin was lower than that of the centre extract and that the copper number (TAPPI 1988) of the pieces of the paper taken from margin is higher than that of the centre.

The copper number indicates that more reducing aldehydes and reactive keto groups are present in the samples taken from the margin than in the samples from the centre. In addition to the visual differences shown in Figures 3.1a-c, this also proves that the fibres had deteriorated more severely at the margin of the papersheets than in the centre.

In the IR spectra obtained, there was a significant difference in the absorption at 1735 cm^{-1}. This band may be due to a range of effects. According to Bellamy (1957), this wavenumber is due to the C=O stretching vibrations of ester carbonyls. Fengel and Wegener (1989) assumed that carboxyl groups are involved whereas in the literature, the band at approximately 1750 cm^{-1} is generally discussed together with those at 1640 cm^{-1} and 1600 cm^{-1}. To assign the cause of the band at 1735 cm^{-1} three experiments were carried out.

Experiment 1

The difference spectrum between the centre and the margin was calculated (see Figure 3.5). Prior to subtraction, the differential spectra were normalised at 2900 cm^{-1}, as it may be assumed that both material matrices contain a similar amount of C-H.

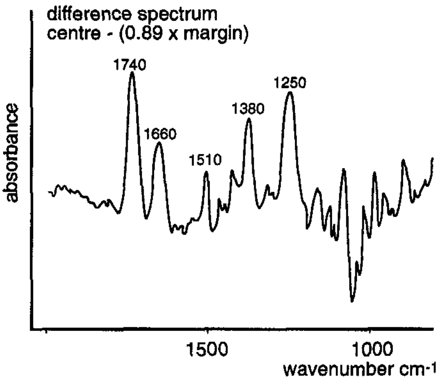


Figure 3.5 Difference spectrum between the margin and the centre of the page of the book

Figure 3.5 shows that the difference spectrum has distinctive bands at 1740, 1660, 1510, 1380 and 1250 cm^{-1}. The strong band at 1660 cm^{-1} may indicate that the centre contains more bound water. It can also be seen that the chemical composition of the fibres taken from the margin are different from those from the centre. The centre has a more aromatic nature (approximately 1510 cm^{-1}), and the bands at 1740 and 1250 cm^{-1} indicate the presence of an ester, moreover there is a difference in the C-H bending vibrations (1380 cm^{-1}).

Experiment 2

Any esters, present in the centre of the sheet, were hydrolysed by exposing the paper to alkaline vapours for 1 minute at 23°C (concentrated NH_3/NH_4OH, Merck p.a.). The material was then exposed for 1 minute at 23°C to acid vapours (concentrated fuming HCl, Merck p.a.).

Thus $R_1COOR_2 + OH^- \rightarrow R_1COO^- + R_2OH$, followed by
$R_1COO^- + H^+ \rightarrow R_1COOH$

A spectrum was recorded after each treatment. The spectra are shown in Figure 3.6.

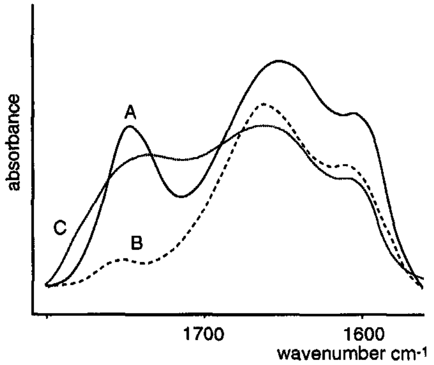


Figure 3.6 *Bands in the range 1600 - 1800 cm^{-1} of the paper taken from the centre of the sheets A: untreated paper; B: paper after exposure to alkaline vapour; C: paper after exposure to alkaline vapour followed by acid vapour*

After exposure to alkaline vapour, the band at approximately 1740 cm^{-1} disappeared. An ammonium carboxylate ester was formed (approximately 1600 cm^{-1}). Upon treatment with hydrochloric acid, it is assumed that the free carboxylic acid is formed. This according to $R_1COOR_2 + {}^-OH \rightarrow R_1COO^- + R_2OH$ and $R_1COO^- + H^+ \rightarrow R_1COOH$.

The possible side reactions $R_1COOR_2 + NH_3 \rightarrow R_1CONH_2 + R_2OH$, followed by $R_1CONH_2 + H_2O \rightarrow R_1COOH + NH_3$, were not observed.

Experiment 3

The following spectral calculations were considered, where S stands for "the IR spectrum of...":

$$S_{book} - S_{cellulose} = S_{[lignin+residue]} \quad (1)$$

$$S_{residue} = S_{[lignin+residue]} - S_{lignin} \quad (2)$$

Using the spectral calculations, the spectrum of the residue ($S_{residue}$) should be similar to that in Figure 3.5, because the ester only should remain if it is assumed that there are no differences in the hemicellulose composition (see Figure 3.7). To obtain these spectra, the reference spectra of native cellulose and softwood lignin were used.

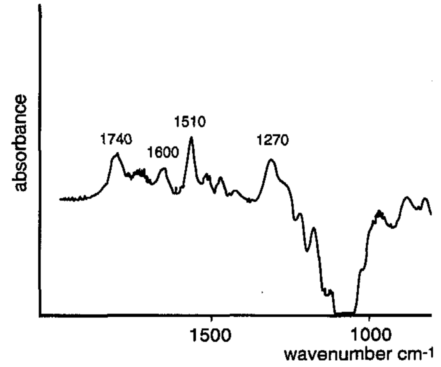
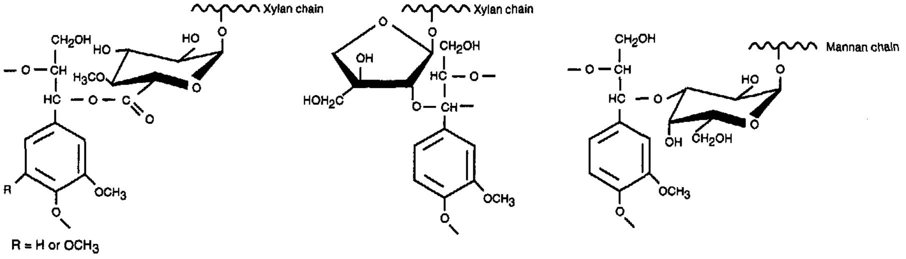


Figure 3.7 *Difference IR spectrum of the residue obtained by subtracting the spectra of model substances,* i.e. *native cellulose and a softwood lignin from the spectrum of the papersheet from the book (centre)*

The difference spectrum obtained in this way is comparable to the spectrum in Figure 3.5. The centre contains a compound or complex that was not found in the margin of the book, and this substance that contains functional ester groups, hydrocarbon groups and aromatic groups.

These bands found in the spectrum for the paper can be explained as follows. The formation of esters and ethers from polysaccharides and lignin is well known. Some models of this reaction have been presented by Fengel and Wegener (1989), and the resulting lignin-polysaccharide complex may contain the following compounds of the ester type (1) and of the ether type (2 and 3 in Figure 3.8).



1. 2. 3.

Figure 3.8 *Possible lignin-polysaccharide complexes, due to the reactions of hemicellulose and lignin according to Fengel and Wegener (1989)*

The ester type compounds are known to be hydrolysed rapidly in an alkaline environment. This fact, combined with the spectra we obtained, enabled us to assume that a *lignin-polysaccharide adduct* occurs in the centre of the book. This type of adduct does not occur, or to a lesser extent, at the margin of sheets of paper coming from the book "Land om land".

3.3.4 The crystallinity of the cellulose

The change in the morphological structure of the cellulose present in the two domains of the paper can easily be calculated from the intensities of the bands at 1372 cm^{-1} and 2900 cm^{-1} (Nelson and O'Connor 1964). This is referred as the crystallinity index (CI) of the cellulose. CI is the ratio of the absorption intensities of the bands at 1372 cm^{-1} and at 2900 cm^{-1}.

The mean value of four measurements of the crystallinity index (CI) are listed in Table 3.2.

Table 3.2 *Average crystallinity indices calculated on basis of the intensities of the absorption bands at 1372 cm^{-1} and 2900 cm^{-1}*

Sample	CI(FTIR)	Standard deviation
Centre	0.51	0.04
Margin	0.44	0.02

From the results obtained, it appears that the fibres taken from the margin of the sheets are less crystalline than those in the centre. This corresponds reasonably well with the results obtained from deuterium oxide exchange experiments, carried out earlier and reported separately in a previous report (Havermans 1991). The higher OD fraction indicates a larger (accessible) amorphous fraction in cellulose.

The calculated OD/OH fractions were:

Centre, OD fraction : 15% (OH fraction = 85%),
Margin, OD fraction : 20% (OH fraction = 80%).

These calculated ratios and fractions indicate that there is not only a chemical difference but also a morphological difference between the centre and the margin. The fibres taken from the centre of the sheet contain more crystalline cellulose than fibres from the margin. This may be explained by a higher extent of natural ageing at the margins, as it has been found that natural ageing results in an increase of the amorphous fraction of paper cellulose, and consequently in a decrease of the crystallinity (Bansa 1979).

To some extent, this finding may indicate that the material was not exposed to high concentrations of air pollution for prolonged periods, as was presented by Porck *et al.* in 1988. Air pollution greatly contributes to acid hydrolysis of cellulose fibres (Lanting and Logtenberg *et al.* 1985; Fellers, Iversen *et al.* 1989; Porck *et al.* 1988) and results in an increase in the crystallinity (Young and Rowell 1986; Fellers, Iversen *et al.* 1989; Sjöström 1993).

Limited effects of air pollution agree with our results of SEM/EDXA measurements of both the margin and the centre. We did not found any measurable amount of sulphur compounds, indicating that absorption of sulphur dioxide did not take place by the paper.

The observed decrease in crystallinity can be explained as follows:

> When cellulose is dehydrated, the bonding and strength properties are generally reduced. The fibres then form larger units and become less accessible to water and the material becomes stiffer. This effect is also known as *hornification* (Jayme 1943). Akim adds the following to this train of thought: "Due to the increase in the amorphous fraction, a glassy stage will be reached during the drying of the fibres, which will eventually lead to horn-formation" (Akim 1978). This shows that the observed effect is likely to be due to poor (dry and hot) storage conditions combined with the raw material (groundwood). Air pollution probably contributes to a lesser extent to the effects observed, although it is known that the presence of air pollutants can accelerate the deterioration of paper.

Another aspect was revealed by studying the spectra of the fibres by combined IR microscopy. Both the spectra obtained from the fibres at the margin and from the fibres in the centre of the pages showed three bands at 1665, 1635 and 1590 cm^{-1}. The last band can be attributed to the presence of aromatic lignin. The band at 1635 cm^{-1} can be attributed to bound water and the band at 1665 cm^{-1} to the presence of carboxyl groups. The acid nature of the book may be due to the presence of carboxyl groups in combination with lignin deterioration products.

3.4 Conclusions

The conclusions from this study are:

- From a chemical and physical viewpoint, the fibres present in the outer regions (margin) of the sheets from the book “Land om Land” differ significantly from the fibres present in the inner regions (centre) of the sheets. The outer regions are more deteriorated:
    a) the fibres present at the margin are shorter than those in the centre,
    b) the amount of reactive aldehyde and keto groups present in the paper from the margin is higher than in that from the centre,
    c) the crystallinity of the centre is higher than that of the margin,
    d) the centre of the paper sheet contains more esters than the margin, possibly as lignin-polysaccharide adducts.
- 'Natural' ageing leads to a decrease in the crystalline structure of the cellulose.
- These results combined with the brittleness of the paper from the edges indicate hornification of the material.
- The ageing process of the book, can be ascribed to bad storage conditions *e.g.* hot and dry.

Acknowledgement

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References

Akim, E. L. (1978).
Changes in Cellulose Structure during Manufacture and Converting of Paper.
Cellulose Chemistry and Technology, ACS Symposium 48, ASC.

ASTM (1971).
ASTM D 778; Hydrogen ion concentration (pH) of buffered paper extracts.

ASTM (1992).
ASTM D 919; Copper number of paper and paperboard.

Banik, G. and J. Ponahlo (1983).
IRS-untersuch der degradierenden Wirkung von Licht und SO_2 auf Pigmentiertes Papier.
Mikrochimica Acta [Wien] 1: 87.

Bansa, H. (1979).
Dauerhaftigkeit von Papier. Source unkown, a copy of this paper is present in the private stock of the author.

Bellamy, L.J. (1959).
The Infra-Red-Spectra of Complex Molecules.
London, Methuen & Co Ltd.

Brown, L., P. Holliday, and I.F. Trotter (1951).
The absorption spectra of some cellulose derivates in the 3-f region.
Journal of the Chemical Society 45: 1532–1539.

Fellers, C., T. Iversen, T. Lindström, T. Nilsson, M. Righdahl (1989).
Ageing/Degradation of Paper, A literature Survey, Report No. 1E.
FoU-projektet for Papperskonservering, Stockholm, Sweden.

Fengel, D. and G. Wegener (1989).
WOOD, Chemistry, Ultrastructure and Reactions.
Berlin, Walter de Gruyter.

Forsskåhl, I. and J. Janson (1992).
Sequential treatment of mechanical and chemimechanical pulps with light and heat. Part 2. FTIR and UV-VIS absorption-scattering spectra.
Nordic Pulp and Paper research Journal 2: 48.

Fuit, C. (1990).
Personal communication.
TNO, Delft, the Netherlands.

Havermans, J. B. G. A. (1991).
Onderzoek naar het karakteriseren van papier en papierveroudering met infrarood-spectroscopie.
PK 91.1118, TNO, Delft, The Netherlands.

Hemmingson, J. A. and H. Wong (1989).
Characterization of Photochemically Degradated Newsprint Solubles by 13C NMR and IR Spectroscopy.
Holzforschung 43: 141.

Hon, D. N. S. (1979).
Photooxidative Degradation of Cellulose: Reactions of the Cellulosic Free Radicals with Oxygen.
Journal of Polymer Science (A: Polymer Chemistry) 17: 441.

Hon, D. N. S. (1984).
Fourier transform IR Spectroscopy and Electron Spectroscopy for Chemical Analyses. Use in the Study of Paper Documents.
Advances in Chemistry Series, Philadelphia, 212, American Chemical Society.

Jayme, G. (1943).
The reactivity of Pulps.
Cellulosechemie 21, 73–86.

Kleinert, T. N. (1969).
Altern und Vergilben von Cellulose.
Holzforschung und Holzverwertung 21: 133.

Lanting, R.W., E.H.P. Logtenberg, J. Muetgeert, H. Nieboer and H.A. Westra (1985).
Veroudering en Aantasting van Cellulose door Luchtverontreiniging.
R 88/145, TNO, Delft, The Netherlands.

Nelson, M. L. and R. T. O'Connor (1964).
Relation of Certain Infrared Bands to Cellulose Crystallinity and Crystal Lattice Type part II. A New Infrared Ratio for Estimation of Crystallinity in Cellulose I and II.
Journal of Applied Polymer Science 8: 1325.

Nelson, M. L. and R.T. O'Connor (1964).
Relation of Certain Infrared Bands to Cellulose Crystallinity and Crystal Lattice Types part I. Spectra of lattice Types I, II, III and of Amorphous Cellulose.
Journal of Applied Polymer Science 8: 1311.

NEN (1981).
NEN 2151; Bepaling van de pH van een waterige suspensie.

Porck, H.J., J. van Heijst, W.J.Th. Smit, I. van Leeuwen (1988)
Research projects within the framework of a national mass conservation in the Netherlands.
Paper Preservation Symposium/Tappi Symposium, Atlanta 74-80.

Porck, H.J. (1990).
Personal communication.

Sjöström, E. (1993).
Wood Chemistry.
Fundamentals and Applications. Boston, Academic Press, INC.

TAPPI (1988).
TAPPI T 430; Copper number of pulp, paper, and paperboard.

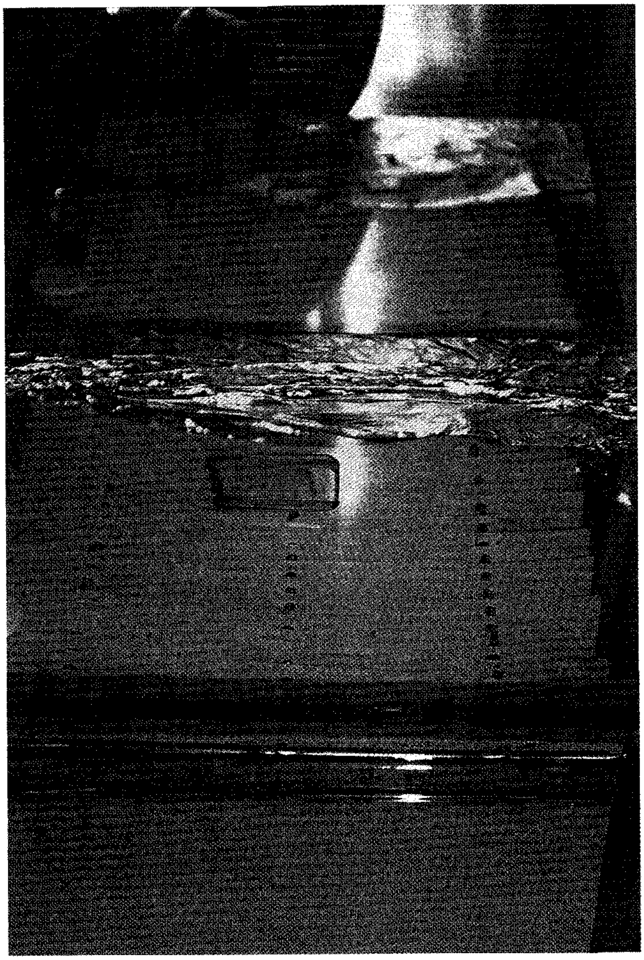
TAPPI (1988).
TAPPI T 509; Hydrogen ion concentration (pH) of paper extracts (cold extraction method).

Young, A. R. and R. M. Rowell (1986).
Cellulose, Structure, Modification and Hydrolysis.
New York, John Wiley & Sons.

Zhbankov, R. G. (1966).
Infrared Spectra of Cellulose and its Derivatives.
New York, Consultants Bureau/Plenum Publishing Corporation.

4

A study of the ageing of paper in normal and inert environments



4. A STUDY OF THE AGEING OF PAPER IN NORMAL AND INERT ENVIRONMENTS

Summary

To determine the extent of ageing during the storage of paper documents in an inert gas, different types of paper were exposed to various conditions in an inert gas (argon) and in oxygen-rich and oxygen-depleted environments. Subsequently, artificial thermal ageing was carried out at 105°C for three days. Chemical, physical and mechanical properties were measured before and after the ageing.

The results of the study demonstrated that the extent of thermal degradation is reduced as the oxygen concentration in the atmosphere is reduced. The discolouration after ageing of lignin-containing paper is less in a more inert environment. Indications were found, that the copper number of the bleached cellulose papers was independent of their calculated absorption coefficients, whereas a relation was found for the lignin-containing paper. In this case the higher the copper number the higher was the absorption coefficient.

Although all the materials exhibited a significant pH reduction after thermal ageing, no significant differences were found related to the extent of "acidification" or to the environment in which the ageing was carried out.

Infrared spectroscopy showed that thermal ageing lowers the crystallinity of the cellulose.

Both the measured folding endurance and the tearing resistance of the papers were lower after artificial ageing and were independent of the environment used. However, the bleached cellulose paper with carbonate as filler deteriorated less in an inert environment.

Finally, it was found that thermal ageing using dry heat only, as described in the standard method ISO 5630/1, causes hornification.

4.1 Introduction

The objective of this study was to contribute to the development of a method for the preservation of archival documents that are consulted only infrequently. The documents are stored for medium-term periods under controlled environmental conditions in an oxygen-depleted environment (Havermans 1993).

The natural ageing of stored paper depends on a number of factors. Clearly, time is the most important parameter in ageing. The different degradation reactions that affect cellulose, and which may be promoted by factors such as temperature and humidity, are time-dependent. As time cannot be influenced, the other degradation factors are normally considered. The temperature is the most important parameter affecting the degradation rate (Atkins 1986; Grassie and Scott 1988; Fengel and Wegener 1989), the reaction rate constant for the degradation being expressed by the Arrhenius equation:

$$k = A \cdot e^{\frac{-E_a}{RT}} \qquad (1)$$

Where k : reaction rate constant ($mol^{-1} \cdot dm^3 \cdot s^{-1}$)

E_a: activation energy ($J \cdot mol^{-1}$)

T : temperature (K)

R : gas constant ($J \cdot K^{-1} \cdot mol^{-1}$)

A : Arrhenius constant, a frequency factor ($mol^{-1}.dm^3.s^{-1}$)

The reaction rate constant, which is highly temperature-dependent, also depends on the circumstances under which the degradation occurs.

Under normal circumstances, the degradation of paper is also greatly affected by the presence of oxygen, moisture and air pollution. If it is assumed that the air pollution is reduced to a minimum in the area where the material is stored, the degradation depends on oxygen and moisture. The following three degradation reactions are then relevant: thermal oxidation, dehydration and depolymerisation.

Thermal oxidation degrades cellulose, particularly in the amorphous regions (Fengel and Wegener 1989; Sjöström 1993). Firstly at increased temperatures, cellulose radicals may form, and these may react with oxygen to produce, for example, hydroperoxide radicals (see Figure 4.1).

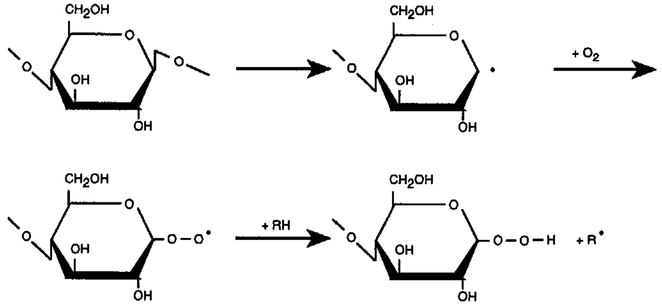


Figure 4.1 The oxidation of cellulose with the formation of hydroperoxide radicals

According to Young and Rowell (1986) oxygen reacts preferentially in the amorphous region, and thermal oxidation will somewhat enhance the fraction of microcrystalline cellulose, an effect similar to that of acid-catalysed hydrolysis.

Secondly, the hydroxyl groups present (C6-alcohol group and C2 and C3 alcohol groups), and the reducing end-groups are easily oxidised (Blazej and Kosik 1985; Fengel and Wegener 1989; Sjöström 1993), to give aldehydes and carboxyl groups. The ring structure of the glucose unit may remain intact. When the C1-H or C4-H bonds are attacked during oxidation, chain rupture will presumably result. Some major end products of this type of degradation include glucuronic acid, gluconic acid and aldaric acid. The thermal degradation of cellulose can also yield 1,6-anhydro-β-D-glucopyranose, and this reaction is used for a synthesis of this compound. This depolymerisation occurs rapidly if the material is exposed to microwave radiation (Straathof, van Bekkum *et al.* 1988).

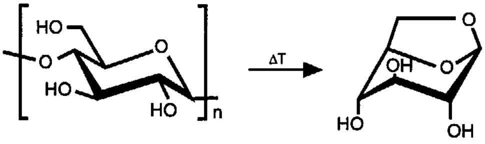


Figure 4.2 Synthesis of 1,6-anhydro-β-D-glucopyranose from (1→4)glucans using microwave radiation (according to Straathof et al., 1988)

Dehydration reactions may also occur, and these may be classified as:

- intermolecular dehydration (cross-linking), and,
- intramolecular dehydration (formation of double bonds, monomers may dehydrate to give furan systems).

Dehydration reactions generally occur in an acid environment, hence this type of reaction is only of secondary interest in these investigations. Depolymerisation, where cellulose breaks up into smaller units under the influence of oxygen and increased temperature, mostly produces 1,6 anhydro-ß-D-glucopyranose, also known as levoglucosan. The structure of possible oxidation fragments which can be formed is given in Figure 4.3.

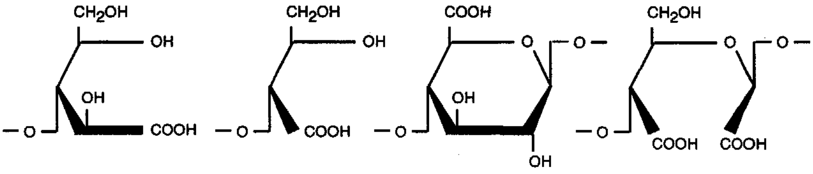


Figure 4.3 *Possible oxidation fragments of cellulose*

This survey of the thermal oxidation of cellulose demonstrates that oxygen can play an important part in the ageing process. The magnitude of this contribution was studied during these investigations.

4.2 Materials and methods

4.2.1 Materials

The materials used in the investigations are listed in Table 4.1.

Table 4.1 *Description of the materials used*

Code	Description
paper-1	Groundwood-containing paper 80 g/m^2. Fibre composition: 77% wood pulp, 23% softwood cellulose; alum/colophonium-sized. Surface-sized with starch.
paper-2	Scripta blanc paper 80 g/m^2, fibre composition: 20 % bleached Kraft softwood cellulose, 60 % bleached Kraft hardwood cellulose, 20% hardwood cellulose; alum/colophonium-sized. Additives approximately 12% calcium sulphate; 1% calcium carbonate; 0.4% sodium carbonate and 4% clay. Surface-sized with starch (Rodenburg 1988).
paper-3	Machine-made softwood sulphite cellulose paper 78 g/m^2, 100% bleached sulphite softwood cellulose. Free from contamination and additives.
inert gas	Argon, AGA Gas, purity 99,8%

All the specimens to be tested were stored at 23°C and 50% RH for at least 3 days before testing. The tests were carried out in glass exposure cabinets with a volume of 32 l in which the paper samples were aged under different conditions. The exposure cabinets were fitted with inlets and outlets for the argon gas. Because of the high density of argon gas (denser than air), the inlet was situated at the bottom of the cabinet and the outlet at the top. The gas flow was monitored using a flowmeter. The exposure cabinets were fitted with covers, and sensors for measuring the temperature and relative humidity were included. Rails were fitted in the cabinets so that the paper could be suspended, in order to allow the separate sheets to hang freely.

4.2.2 Response times

The response time was defined as the period within which the system reached a steady-state condition. The response times for both the relative humidity and the oxygen level in the system were determined before the actual artificial ageing was carried out.

The relative oxygen and/or relative humidity (RH) response time can be defined as the period, measured from the time the flow of argon was turned on to the time when the relative oxygen concentration $[O_2]$ and/or the RH in the cabinet remained constant and approached zero (0).

The response times of both empty cabinets and of cabinets filled with paper were determined at 23°C. The changes in O_2 and RH were recorded from the initiation of the argon flow until the O_2 remained constant. The measured concentrations and times were used to calculate a curve from which the start of the artificial ageing was determined.

Figure 4.4 illustrates the response times. It shows the calculated response of the change in O_2 and RH as a function of time ($[O_2]_{rel}$ and RH respectively). The response value was calculated as the actual measured value expressed as a decimal fraction of its start value. For example when the initial RH was 30% and after 50 minutes it was only 4.8%, then the response at this time was $4.8/30 = 0.19$. The argon flow rate expressed as the number of times the empty exposure cabinet was purged was 6 h^{-1}. The response time to reduce the O_2 from 1 to 0.03 was 50 minutes. The response time of the RH was 80 minutes. The response level of 1 in Figure 4.4 means the maximum oxygen concentration or RH present in the ambient air used. Similar response times were found after filling the exposure cabinet with 30 sheets of paper (A4 size). Therefore the artificial ageing was started after 60 minutes.

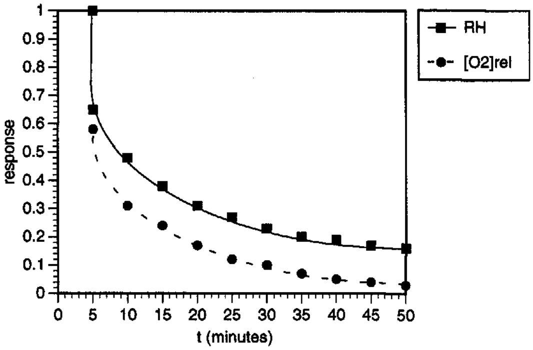


Figure 4.4 *The reduction of the relative oxygen concentration and the relative humidity as a function of time after admitting argon to the system*

4.2.3 Artificial ageing

Methods for the accelerated ageing of paper are standardised. The method chosen for this research was based on the ISO 5630/1 method for thermal ageing of paper for three days at a temperature of 105°C .

The following experiments were carried out:

a) A standardised artificial ageing using ambient air (approximately 20% oxygen) according to the ISO 5630/1 method. This process is hereinafter denoted the *thermal ageing (t).*

b) An artificial ageing using pure argon gas as an inert environment. The argon gas was allowed to flow continuously through the system during the ageing period. After the papers had been placed into the cabinets, the cabinets were purged with argon for at least 60 hours at a temperature of 23°C. Subsequently, the temperature was increased to 105°C and maintained at that temperature for 3 days. This process is denoted the *inert ageing (i).*

c) An artificial ageing using a so-called oxygen-depleted environment. After the paper had been placed into the cabinet, it was purged with argon for one hour at 23°C, after which the temperature was raised to 105°C. The materials were then subjected to thermal ageing at 105°C for 3 days. This ageing process is referred to as the *depleted ageing (e).*

Codes were assigned to the various materials tested to facilitate the interpretation of the results and are listed in Table 4.2.

Table 4.2 Experiments and their codes

description	conditions	code	example
Original values (reference)	storing at 23°C and 50% RH	paper number & r	1r
Thermal ageing	3 days at 105°C/Air	paper number & a	1a
Thermal ageing in an inert gas	3 days at 105°C/Argon	paper number & i	1i
Thermal ageing in a depleted environment	3 days at 105°C/Argon/Air	paper number & e	1e

4.2.4 Analyses

Before and after the artificial ageing, analyses were performed on the materials used. To determine the acidity, the pH of the cold-water extracts of the paper according to TAPPI T 509 (TAPPI 1988) was measured, as deterioration can lead to carboxylic groups. Conductive deterioration products were observed by determining the conductivity of the same cold-water extract. The copper number was measured according to TAPPI T 430 (TAPPI 1988). It is a measure of the reducing aldehydes and reactive keto groups and therefore indicates the amount of degradation. Physical changes of the paper were assessed by measuring the equilibrium moisture content (mc) of the papers according to TAPPI T 412 (TAPPI 1990). The artificially aged papers were studied after 3 days reconditioning at 23°C and 50% RH. The change in the mc indicates a change in the cellulose structure (crystalline cellulose contains less bound water than amorphous cellulose). The change in optical reflectance was measured using diffuse reflectance spectrophotometry at 457 nm according to ISO 2471 (ISO 1977), which may indicate the formation of double bonds during ageing. From the measured values, the value of the quotient of the absorption coefficient divided by the scattering coefficient (k/s) of the sample was calculated as given by the Kubelka-Munk equation

$$\frac{(1-(S/R))^2}{2\cdot S/R}=\frac{k}{s} \tag{2}$$

Here S is the reflectance of the sample and R the reflectance of the reference material according to the calibration procedure given in ISO 2471. The calculated absorption coefficient, k, and the scattering factor, s, are both depending on the particle size and refractive index of the sample to be investigated (van den Akker 1949; Hope Allen and Goldfinger 1972).

Infrared absorbance spectra obtained by using Fourier transform infrared spectroscopy were determined on the bleached sulphite softwood cellulose paper (paper-3) only from

400 to 4000 cm^{-1}. The spectra were analysed with regard to the presence of carboxyl and or carbonyl groups, and the crystallinity index was calculated using the absorption bands at 1374 and 2900 cm^{-1} (Nelson and O'Connor 1964; Havermans 1991).

The performance of the paper was followed with regard to two mechanical properties: the tear resistance of the paper according to TAPPI 414 om-88 and the folding endurance according to SCAN P-17 with the Köhler Molin (loading 250 g).

4.3 Results and discussion

The chemical changes in the materials used are shown in the Figures 4.5, 4.6 and 4.7.

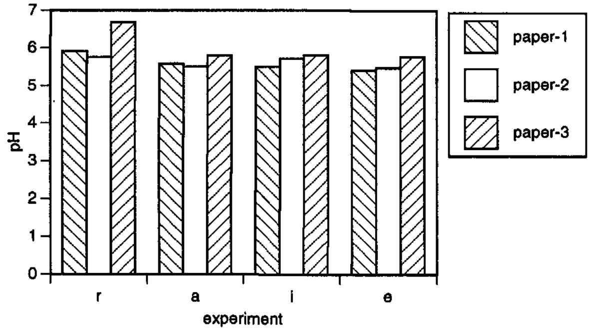


Figure 4.5 *The pH of the cold-water extract of the three papers before ageing (r), and after thermal ageing (a), thermal ageing in an inert gas (i) and thermal ageing in a depleted environment (e)*

As can be seen in Figure 4.5, papers 1 and 2 were acid (the initial pH of the cold-water extract was 5.9 and 5.8 respectively) while the pH of the of the cold-water extract of paper-3 was close to neutral (pH = 6.7). After the thermal ageing (a), all three papers were more acidic especially the pure cellulose paper (the pH dropped from 6.7 to 5.8). This indicates that carboxylic compounds were formed during the thermal ageing. Under an inert atmosphere (i), the pH of paper-2 (Scripta Blanc) remained unchanged while both papers 1 and 3 became more acidic. After the depleted ageing (e), the pH of all three papers was affected. All papers became more acidic, indicating that acidic compounds were formed during the ageing process.

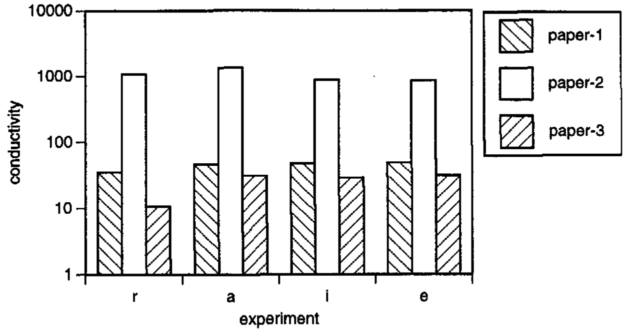


Figure 4.6 *The conductivity of the cold-water extract of the three papers before ageing (r), and after thermal ageing (a), thermal ageing in an inert gas (i) and thermal ageing in a depleted environment (e)*

From the conductivities of the cold-water extracts used for the pH measurements, shown in Figure 4.6, it was found that the initial conductivity of paper-2 was very high compared to that of paper-1 and paper-3. This can be attributed to the inorganic additives used in paper-2 that partly go into solution. While the conductivities of the extracts of both paper-1 and paper-3 increased during the ageing in an inert or oxygen-depleted environment, the conductivity of paper-2 decreased. This can be attributed to a dissociation or decomposition of carbonates present in paper-2 and a reduction in the amount of soluble inorganic compounds. Only in the case for the pure cellulose-containing paper-3, the conductivity of the cold-water extract after inert ageing significantly lower than after the other types of ageing. It may be concluded that fewer deterioration compounds were formed during ageing in an inert atmosphere.

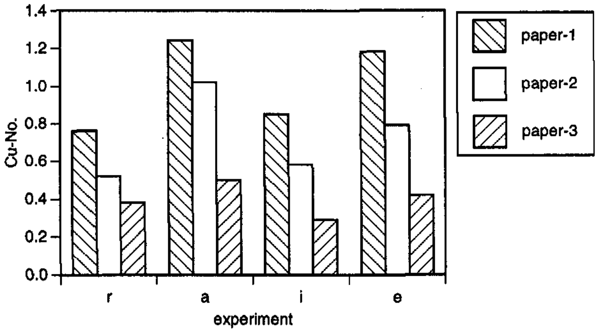


Figure 4.7 *The copper number of the three papers before ageing (r), and after thermal ageing (a), thermal ageing in an inert gas (i) and thermal ageing a depleted environment (e)*

An important result is the change in copper number of the papers. Figure 4.7 shows the increase of the copper number after thermal ageing (a) for all the papers used. The increase suggests that, in these papers reducing aldehydes and reactive keto groups are formed, and thus that an oxidative deterioration has taken place. As expected, the amount of these deterioration products was less after the inert ageing (i). The copper number was higher after the depleted ageing (e), but this effect was lower than that observed after the ageing in the oxygen-containing environment.

With regard to the physical changes in the papers, it was shown that the equilibrium moisture content of the papers at 23°C and 50% RH was lowered after the ageing experiments (see Figure 4.8). The equilibrium moisture content of the unaged papers did not differ from the papers, purged 60 hours with argon at 23°C and reconditioned for 3 days at 23°C and 50% RH, therefore the reference (r) values of the untreated papers are given in Figure 4.8. The effect of the inert gas was small. In both the inert ageing (i) and the depleted ageing (e), the moisture contents of both paper-1 and paper-2 decreased more than during thermal ageing (a). The moisture content of paper-3, the pure cellulose paper, remained almost constant during these different types of ageing. The results indicate a morphological change of the paper structure which was not reversed after a recovery time of 3 days (at 23°C and 50% RH). It seems that this "hornification" is more pronounced without oxygen than with oxygen. This may be attributed to the system used: continuously purging with argon. This means that the materials were very dry throughout the ageing.

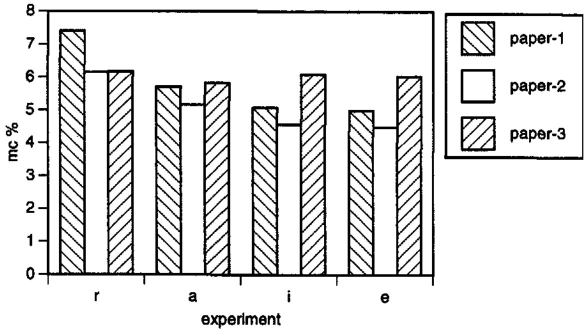


Figure 4.8 The moisture content of the three papers before ageing (r), and after thermal ageing (a), thermal ageing in an inert gas (i) and thermal ageing in a depleted environment (e)

The brightness and the calculated Kubelka-Munk coefficients of the papers before and after the ageing experiments are shown in Figures 4.9 and 4.10. It was found that the brightness of the thermally-aged paper-1, containing groundwood, was reduced significantly less in an inert atmosphere than in the oxygen-rich or depleted environment. These changes are expressed more clearly in the change in the quotient k/s calculated by the Kubelka-Munk equation. In Figure 4.10, the increase in k (assuming s is constant) is shown by comparing the k/s value for each ageing experiment by the k_r/s_r value of the unaged paper (thus the y-axis is representing k/k_r).

If it is assumed that the scattering coefficient is largely unchanged by the ageing and that all changes are in the absorption coefficient, than this figure shows that the amount of chromophore groups increased during the ageing. The use of an inert environment somewhat reduces the amount of chromophores produced especially in the wood-containing paper-1.

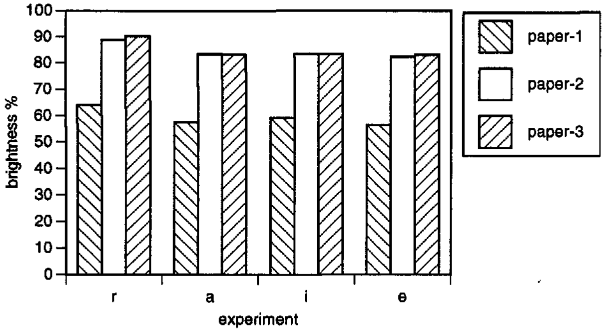


Figure 4.9 *The brightness of the three papers before ageing (r), and after thermal ageing (a), thermal ageing in an inert gas (i) and thermal ageing in a depleted environment (e)*

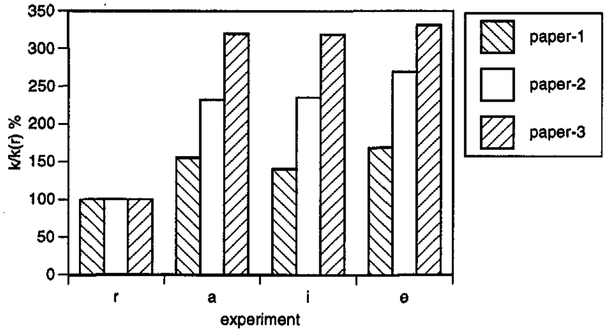


Figure 4.10 *The retention of the calculated Kubelka-Munk values of the three papers before ageing (r), and after thermal ageing (a), thermal ageing in an inert gas (i) and thermal ageing in a depleted environment (e)*

To have a closer look in the ageing behaviour of lignin-containing papers compared to the woodfree papers, the brightness is compared to the copper number. If the calculated k/s-value is plotted against the copper numbers (see Figure 4.11), it becomes clear that the papers containing bleached cellulose, *i.e.* paper-2 and paper-3, did not change in brightness although the copper number changed. For the bleached papers it is therefore concluded that the brightness is almost independent of the amount of reducing aldehydes and reactive keto groups formed in the papers. Thus for cellulose, ageing will change the copper-number, but it will (almost) not affect its brightness.

For the groundwood-containing paper a relation is found: the higher the copper number the higher the k/s value, and therefore the higher the absorption coefficient, assuming that s is unchanged. This must be attributed to the presence of lignin. In the aromatic lignin structure, chromophore groups can be formed much easier than in cellulose. Thus the presence of lignin in paper will cause discolouration during thermal ageing. This discolouration can be related to the aldehyde and keto groups formed during ageing. Thus discolouration tells us that a deterioration took place, however deterioration will not always result in discolouration.

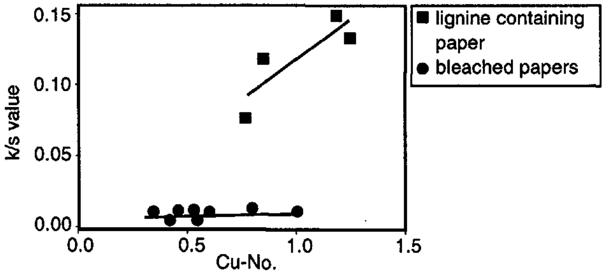


Figure 4.11 *The calculated k/s-value vs. the copper number for the lignin containing paper, paper-1 and the bleached (woodfree) papers, paper-2 and paper-3*

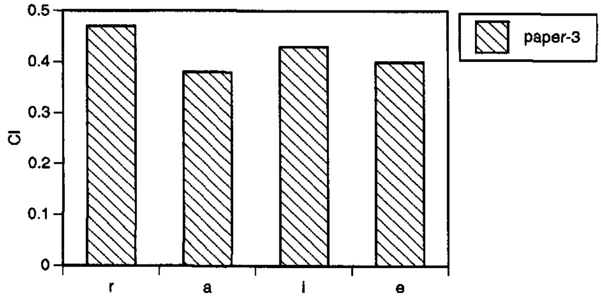


Figure 4.12 *The calculated crystallinity index for the pure bleached softwood cellulose paper, paper-3, based on the absorption bands at 1372 and 2900 cm^{-1}, before (3r) and after thermal ageing using standard conditions (3a), an inert (3i) and a depleted (3e) environment*

The FTIR spectra showed that a band appeared at 1737 cm^{-1} in the case of paper thermally aged under standard conditions, but that in the spectrum for the unaged paper, this band was not present. This indicates that carbonyl and/or carboxyl groups are present after the ageing. In the spectra of the papers aged in an inert and in an oxygen-depleted environment, this band was absent. This confirms that the deterioration of cellulose is less during storage in an inert environment.

Figure 4.12 shows that the calculated crystallinity index decreased on ageing (see also section 2.3). This effect is in harmony with earlier studies on the natural ageing of paper (for example: Havermans 1991). More amorphous cellulose was apparently formed during the thermal ageing. However, the reduction in crystallinity was less for the aged paper under an inert environment than for the papers aged under a normal or oxygen-depleted environment ($\Delta CI_i < \Delta CI_e < \Delta CI_a$).

The mechanical properties of the papers before and after the ageing experiments were determined in the two principal directions: the machine direction (MD) and the cross machine direction (CD). From these values, the geometric mean of the properties X was calculated according $X_{gm} = \sqrt{X_{MD} \times X_{CD}}$. The geometric mean value X_{gm} corresponds to the value for an isotropic sheet, and its use facilitates the comparison of sheets with different mechanical anisotropies.

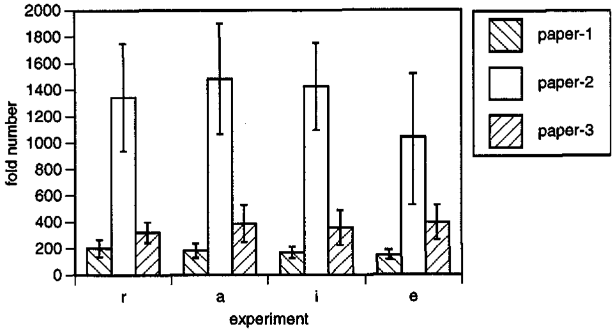


Figure 4.13 *The geometric mean value of the fold number of the three papers before ageing (r,) and after thermal ageing (a), thermal ageing under an inert gas (i) and thermal ageing under a depleted environment (e). The standard deviation of the measurements is also indicated*

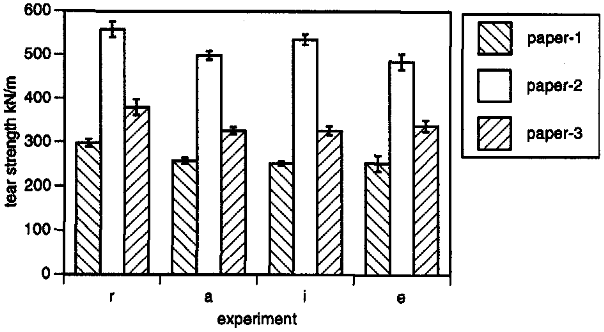


Figure 4.14 The geometric mean value of the tear strength in kN/m of the three papers before ageing (r) and after thermal ageing (a), thermal ageing under an inert gas (i) and thermal ageing under a depleted environment (e) The standard deviation of the measurements is also indicated

The fold number (Figure 4.13) indicates no significant difference between the aged and unaged papers. However indications were found that the fold number for the pure sulphite paper-3 increased somewhat due to the ageing. These ageing phenomena can be described as being due to a relaxation of the fibres in the paper (Iversen 1992). The tear strength (see Figure 4.14) show that the tear strength decreased due to ageing. However, for paper-2 aged in an inert environment, this decrease was less than for the other two papers studied.

The reduction in the crystallinity in combination with the reduction in the moisture sorption and the loss of strength indicate that artificial ageing using heat only results in a structural change in the cell wall due to an irreversible bonding of cellulose surfaces causing a loss in strength (Jayme 1944; Akim 1978). The fibrils aggregated into larger units on drying, and this reduces the area accessible to water. This effect is sometimes called "hornification". As oxygen reacts preferentially in the amorphous region of cellulose, or preferably with the hemicellulose, this effect therefore occurs more severely in wood-containing paper, as it contains more amorphous material. Therefore, thermal oxidation somewhat enhances the hornification of paper by lowering the fraction of crystalline cellulose. The theories of Young and Powell should therefore be reconsidered.

4.4 Conclusions

The following conclusions can be drawn from the results of these investigations into the effects of ageing on paper stored in an inert environment.

- The degradation of paper is slowed down by storage in an inert environment. This is especially the case for the lignin-containing paper.
- In this study, the acidification of the paper was not affected by the ageing conditions used.
- Thermal ageing using dry heat only, prescribed in the standard method ISO 5630/1, causes hornification.
- Indications were found that the hornification of paper increased more when the paper was stored in an inert environment at high temperatures than when it was stored under standard ageing conditions with ambient air.
- As a result of the thermal ageing, the mechanical strength of the papers was reduced. This was independent of the environment used. However, the reduction was less in the case of the carbonate-containing paper when the ageing was carried out in an inert environment.
- The formation of reducing aldehydes and reactive keto groups in the bleached cellulose-containing papers was independent of their change in brightness indicated by their calculated absorption coefficients. However, in the case of the lignin-containing paper, a relation was found showing that the absorption coefficient increased with increasing copper number.
- Discolouration tells us that a deterioration took place, however deterioration will not always result in discolouration.
- From FTIR spectra, it was concluded that the oxidation of cellulose is reduced significantly when the paper is stored in an inert atmosphere. Paper thermally aged according to the standard method, 3 days at 105°C in an oven, showed a deterioration in its morphological structure similar to that of naturally aged paper.

Acknowledgement

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References

Akim, E.L. (1978).
Changes in Cellulose Structure during Manufacture and Converting of Paper.
Cellulose Chemistry and Technology, ACS Symposium 48, ASC.

Atkins, P.W. (1986).
Physical Chemistry.
Oxford, Oxford University Press.

Blazej, A. and M. Kosik, Ed. (1985).
Degradation Reactions of Cellulose and Lignocellulose.
Cellulose and its Derivates. New York, John Wiley & Sons.

Fengel, D. and G. Wegener (1989).
WOOD, Chemistry, Ultrastructure and Reactions.
Berlin, Walter de Gruyter.

Grassie, N. and G. Scott (1988).
Polymer Degradation and Stabilisation.
Cambridge, Cambridge University Press.

Havermans, J.B.G.A. (1991).
Onderzoek naar het karakteriseren van papier en papierveroudering met infrarood-spectroscopie.
PK 90.1118.
TNO, Delft, The Netherlands.

Havermans, J.B.G.A. (1993)
Invloeden van het milieu op de houdbaarheid van papier.
De Restaurator, 23, 6-15.

Hope Allen, E. and G. Goldfinger (1972).
The Color of Absorbing Scattering Substrates. I. The Color of Fabrics.
Journal of Applied Polymer Science 16: 2973.

ISO (1977).
ISO 2471; Paper and board - Determination of opacity (paper beacking) -
Diffuse reflectance method.

Iversen, T. (1992).
Personal communication concerning the relaxation of cellulose molecules.

Jayme, G. (1944).
Hemicelluloses and their utilization.
Wochenblatt fur Papierfabrikation, 42: 295–304.

Nelson, M.L. and R.T. O'Connor (1964).
Relation of Certain Infrared Bands to Cellulose Crystallinity and Crystal Lattice Type part II. A New Infrared Ratio for Estimation of Crystallinity in Celulose I and II.
Journal of Applied Polymer Science 8: 1325.

Nelson, M.L. and R.T. O'Connor (1964).
Relation of Certain Infrared Bands to Cellulose Crystallinity and Crystal Lattice Types part I. Spectra of lattice Types I, II, III and of Amorphous Cellulose.
Journal of Applied Polymer Science 8: 1311.

Rodenburg, L.J.M. (1988).
ACBAM Phase 4: Measurements of the depostition-rates of some cellulose containing materials. R 88/179a.
TNO, Delft, The Netherlands.

Sjöström, E. (1993).
Wood Chemistry. Fundamentals and Applications.
Boston, Academic Press, INC.

Straathof, A.J.J., H.v. Bekkum and A.P.G. Kieboom (1988).
Preparation of 1,6-Anhydroglucose from (1-4)-Glucans using Microwave Technology.
Recueil des Travaux Chimiques des Pay-Bas 107: 647.

TAPPI (1988).
TAPPI T 430; Copper number of pulp, paper, and paperboard.

TAPPI (1988).
TAPPI T 509; Hydrogen ion concentration (pH) of paper extracts (cold extraction method).

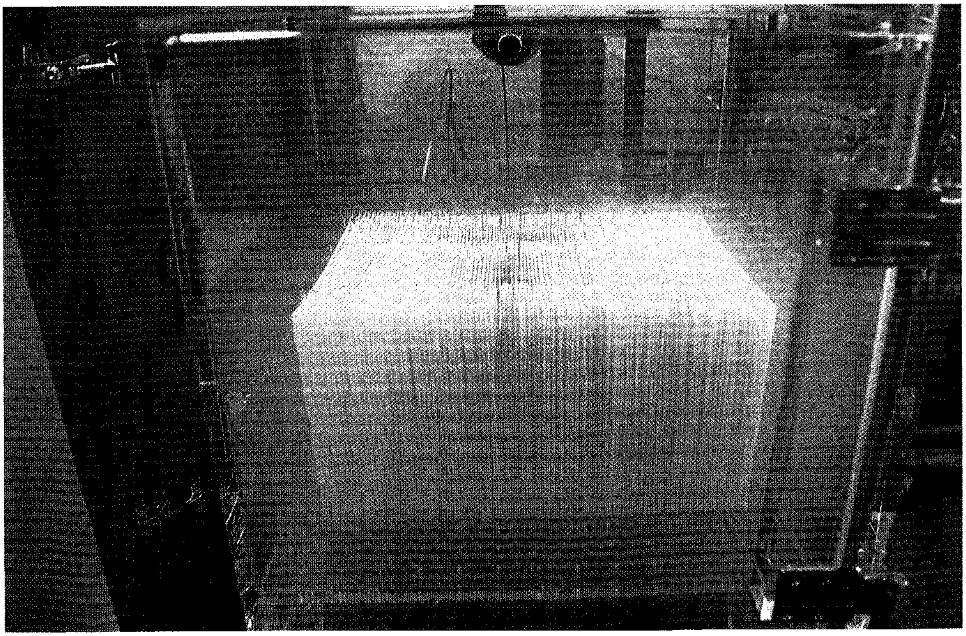
TAPPI (1990).
TAPPI T 412; Moisture in paper and paperboard.

Van den Akker, J.A. (1949).
Scattering and absorption of light in paper and other diffusing media.
Tappi Journal, 32(11): 498.

Young, A.R. and R.M. Rowell (1986).
Cellulose, Structure, Modification and Hydrolysis.
New York, John Wiley & Sons.

5

Influences of SO_2 and NO_x on the accelerated ageing of paper



5. INFLUENCES OF SO_2 AND NO_X ON THE ACCELERATED AGEING OF PAPER

Summary

Pure cellulose-made papers as well as commercial papers were thermally aged (12 days at 90°C and 50% relative humidity (RH), or artificially polluted using two conditions: (i) 4 days to 10 ppm SO_2 and 20 ppm NO_x; (ii) 14 days to 10 ppm SO_2 and 20 ppm NO_2; and followed by thermal ageing. NO_x is here the total concentration of NO_2 and NO. These treatments led to different levels of deterioration.

Chemical, physical and mechanical changes in the materials were measured and evaluated, and the relative deterioration rates were calculated for the different types of papers used.

It was concluded that the ageing of paper was faster when the air pollutants are present. Also it was found that the deterioration occurring during thermal ageing differs from the deterioration in the presence of the air pollutants. For alkaline papers the absorption of NO_x was accompanied by the formation of nitrates.

The acid papers showed a relative deterioration rate similar to that of the groundwood-containing paper. These rates were similar to that of pure bleached sulphite softwood, and therefore groundwood, *i.e.* lignin-containing papers, are not recommended for long-term storage. Alkaline papers showed a good resistance against acid attack, although they did deteriorate to a great extent when thermal ageing only was used.

It is recommended that additional studies are carried out on the deterioration products related to the kinetics, to provide a better understanding of the deterioration processes that take place in paper. In these studies other relevant air pollutants, *e.g.* ozone and acetic acid should be included.

5.1 Introduction

Accelerated ageing tests on paper have been performed already for more than 50 years, aiming at a good prediction of the life expectancy of the paper used (Priest 1994). Strictly speaking, the only way to evaluate the durability of a material or a method of improving paper permanence is to store the treated paper under relevant conditions for a long time, perhaps for several hundred years. Such natural ageing is however highly impractical, and some form of accelerated ageing is therefore desirable. The International Standard Organisation (ISO) 5630 standard, "Paper and Board–Accelerated Ageing", presents four different treatments: dry heat treatment at 105°C, 120°C or 150°C, and moist heat treatment at 90°C and 25% relative humidity (RH) or at 80°C and 65% RH. In a round robin test involving members of the ISO TC6/SC2/WG12 working group, it was noted that about the same deterioration was found after 12 days at 90°C and 50% RH as after 24 days at 80°C and 65% RH. (Kolseth 1992). An accelerated ageing method was needed for the successful completion of the present study. The use of the Arrhenius method can give a reaction rate or deterioration rate. However, to measure the rate of change of some property at a certain temperature requires many experiments to give an acceptable answer, and criticism of the method has centred on the inherent need for extrapolation (Priest 1994) especially when air pollutants are involved. Another approach was therefore chosen for this study: thermal ageing and pollution experiments are carried out sequentially with thermal ageing both before and after the pollution.

The thermal ageing method should, if possible, yield useful results related to the degradation of paper in not more than a few days. Ageing for 12 days at 90°C and 50% relative humidity was therefore chosen.

Deterioration using air pollutants is not yet described by standardised methods, but the effects of air pollutants were investigated previously by several researchers (Kimberly 1932; Lyth Hudson and Milner 1961; Lyth Hudson, Grant *et al.* 1964; Lyth Hudson 1967; Daniel, Flieder *et al.* 1990; Havermans 1990; Iversen and Kolar 1991; Banik, Sobotka *et al.* 1993) as described in chapter one of this thesis. It was decided to combine thermal accelerated ageing with the pollution of the paper, since only by combining the deterioration and ageing steps does it seems possible to answer, in a reasonable limit of time and experiments, the basic question as to the durability expectation of a paper.

From the literature it is known that the acid-catalysed hydrolysis of cellulose can be considered to be a first order hydrolysis reaction (Daruwalla and Shet 1962; Springer 1966; Young and Rowell 1986). For a simple reaction such as $A \rightarrow P$, with the concentrations $[A]$ and $[P]$, the reaction rate can be expressed as:

$$rate = \frac{d[P]}{dt} = -\frac{d[A]}{dt} = k \cdot [A] \tag{1}$$

which gives:

$$\ln\left(\frac{[A_0]}{[A_t]}\right) = k \cdot t \tag{2}$$

In our case a direct calculation of the rate coefficient k for cellulose decay was not possible, because a limited number of experiments was available. It is however possible to calculate the factor ($k \cdot t$) according to:

$$\ln\left(\frac{[P_t]}{[P_0]}\right) = k \cdot t \tag{3}$$

Where:

$[P_0]$ is the concentration of degradation products present at t=0 or the reference $[P_r]$, and $[P_t]$ is the concentration of degradation products after each type of experiment.

From different deterioration experiments, a deterioration sequence can be obtained, for example thermal ageing deteriorates paper less than pollutants do when present on paper in saturation concentration. From the deterioration level sequence, the following data can be derived for each paper, where deterioration level 0 can be seen as the value of the untreated paper (Table 5.1).

Table 5.1 *An example of monitoring the relative deterioration rate*

Deterioration level	ln $[P_t]/[P_0]$	k·t
0	ln $([P_0]/[P_0])$	$(k \cdot t)_0 = 0$
1	ln $([P_1]/[P_0])$	$(k \cdot t)_1$
2	ln $([P_2]/[P_0])$	$(k \cdot t)_2$
3	ln $([P_3]/[P_0])$	$(k \cdot t)_3$

This approach makes it easy to compare different papers and/or treatments with each other using for example a pure cellulose as the reference. For each experiment type, the calculated k·t-values for each type of paper are plotted versus the corresponding k·t-values for this reference paper. In this way all the papers can be compared on the basis of their relative reaction rate. Theoretically, this will give a line through the origin, its slope being the relative rate of deterioration. A major question remains: what reaction products should be used to obtain values for ln $([P_t]/[P_0])$.

If the assumption of a first order acid catalysed hydrolysis is valid, the hydrolysis of the 1,4-glucosidic linkage will result in a shortening of the cellulose chain to produce fragments, having molecular weights lower than that of the untreated cellulose. For pure cellulose, this can be determined by measuring the degree of polymerisation. However, the standard procedure for measuring the degree of polymerisation using for example the viscosity (DP_v) of cellulose fails in the presence of lignin (Browning 1967; TAPPI 1985).

Besides hydrolysis, oxidation may occur, since a combination of a reducing (SO_2) and an oxidizing (NO_x) gas is used for the experiments. Therefore the amounts of reactive aldehyde and/or keto groups can also change, and this change can be followed by the copper number (TAPPI 1988). For pure cellulose there is a good relation between the viscosity (or fluidity) and the copper number, or carbonyl group content (Birtwell, Clibbens *et al.* 1926; Martin, Smith *et al.* 1941).

The degradation of cellulose with acids will yield products that are soluble in alkali. The alkali-soluble fraction of cellulose degraded by oxidation (oxycellulose) is more soluble at lower temperatures than acid-hydrolysed cellulose (hydrocellulose) (Ott 1943). By using *e.g.* the alkali-extractable fraction (AEF) and/or total organic compounds (TOC) that can be extracted in water, both obtained from the different deterioration experiments, the relative rate of deterioration can be calculated by setting [P] = AEF, as shown in the example in Table 5.2.

Table 5.2 *An example of the calculation of the relative deterioration rate*

Experiment	$[P_0]$	$[P_t]$	$[P_t]/[P_0]$	$k \cdot t$
reference	7.3	7.3	1.00	0.00
aged	7.3	9.7	1.33	0.28

Using this approach, it is possible to investigate the artificial ageing behaviour of different types of cellulose and of paper using the air pollutants SO_2 and NO_x. NO_x is here the total concentration of $NO + NO_2$.

This chapter describes this ageing behaviour using both thermal ageing and artificial pollution (with 10 ppm SO_2 and 20 ppm NO_x). This study was a part of a European research project on the effects of air pollutants on the accelerated ageing of paper (Havermans, van Deventer *et al.* 1994) and was published first in the research report of that project.

5.2 Materials used

To understand the behaviour of cellulose fibres used in paper, it is necessary to know the exact paper composition. Also, to reduce the large number of reactions that can take place, two papers without sizing, fillers or other additives were included. Acid woodfree and groundwood-containing papers were included to evaluate the deterioration of papers already stored in *e.g.* libraries and archives. Finally, to judge papers that will be stored in the near future, alkaline papers meeting the suggested standards for paper permanence were included. In Table 5.3, the selected papers are presented. The codes used are comparable to the codes used in the EC STEP project (van Deventer, Havermans *et al.* 1994).

Table 5.3 *The selected materials*

Paper code ***Name***	**g/m²**	**Description**	**Fibre composition**
paper-1 *Sulphite*	78	Bleached sulphite softwood cellulose, no fillers, no sizing. The bleaching sequence was DEHD where the first D was treatment with chlorine dioxide, ClO_2, at low (30°C) temperature and pulp consistency (3%). E was alkaline extraction with sodium hydroxide, NaOH. H was hypochlorite treatment (NaOCl) and finally D was a chlorine dioxide treatment at elevated temperature (60°C) and higher consistency (10%).	100% softwood
paper-2 *Linters*	76	Cotton linters cellulose, no fillers, no sizing The cotton linters paper was made of linters bleached with elemental chlorine and hypochlorite.	>95% cotton
paper-3 *Acid mechanical*	80	Groundwood-containing, alum-rosin sized. From the ash content and an elemental analysis using the SEM/EDXA technique, it was concluded that it contained approx. 22% kaolin clay.	75% groundwood 25% softwood
paper-4 *Archive*	80	Archive quality permanent paper, approximately 3% $CaCO_3$ The cambers were bleached with H_2O_2. The watermarks were produced using a dandy roll. Polyvinyl alcohol was added (impregnation + size press) as a dry strength agent.	100% cotton
paper-5 *Alkaline copy*	80	Alkaline copy paper, approximately 6% $CaCO_3$ Methyl ethyl cellulose was used as a dry strength additive (size press addition approx. 4%).	50% softwood 50% hardwood
paper-7 *Acid copy*	80	Acid copy paper, approximately 18% kaolin clay, alum-rosin sized Starch was used as a dry strength additive (size-press addition). Softwood and hardwood cellulose and kaolin (Al-compounds) were identified.	40% softwood 60% hardwood

5.3 Experimental

Two experimental pollution set-ups were used. At TNO and at the Centre de Recherches sur la Conservation des Documents Graphiques (CRCDG), France, papers were polluted at 23°C and 50% relative humidity. At TNO, a 4 day pollution was used, while at CRCDG a 14 day pollution was used, because it was shown in previous research that two experimental set-ups gave different deterioration effects (Havermans 1992). It was suggested that, at TNO, the acids (H_2SO_4 and HNO_3) were formed and that an acid deposition therefore took place on the papers, *i.e.* the gases SO_2 and NO_x reacted first to form their acids before the paper absorbed them, whereas at CRCDG a dry deposition took place, *i.e.* the gases SO_2 and NO_x were absorbed first, before the reaction to their respective acids took place.

At TNO, samples for artificial pollution were placed in an exposure cabinet made of Plexiglas (polymethylmethacrylate, PMMA), Figure 5.1. The air pollutants were added using mass flow controllers in order to obtain a precise concentration level in the pollution cabinet. The temperature and relative humidity were regulated by an air flow under the same conditions established by placing the cabinet in a controlled climate chamber. The temperature and humidity in the climate chamber were controlled to obtain and maintain a climate of 23±0.5°C and 50±5 % RH.

The floor of the pollution cabinet, through which the air mixed with air-pollutant gases entered, was perforated, and an almost laminar air flow could be obtained, as shown in Figure 5.2. However, in order to ensure that the climate and the concentration of the added air pollutants were uniform throughout the cabinet, the (polluted) air was recirculated using a fan. The ventilation rate in the pollution cabinet was approximately 1 h^{-1} (one exchange per hour).

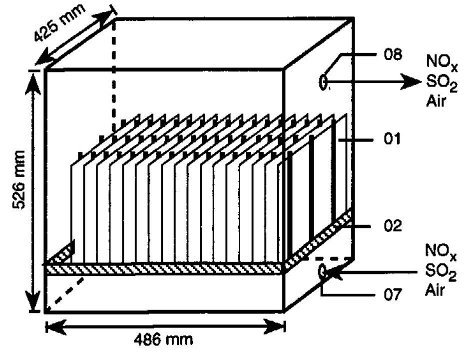
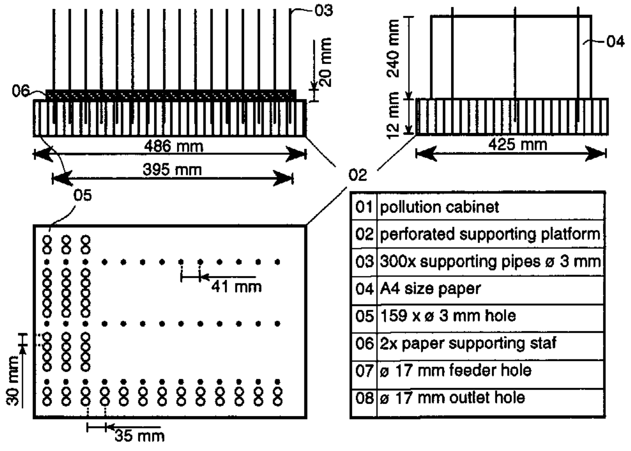


Figure 5.1 *Outline of the TNO artificial pollution cabinet (The explanation of the numbers used is given in Figure 5.2)*



01	pollution cabinet
02	perforated supporting platform
03	300x supporting pipes ø 3 mm
04	A4 size paper
05	159 x ø 3 mm hole
06	2x paper supporting staf
07	ø 17 mm feeder hole
08	ø 17 mm outlet hole

Figure 5.2 *Drawing of the removable bottom plate of the artificial pollution cabinet*

Inside the artificial pollution cabinet, three rows of Plexiglas pillars were placed at intervals of 4 mm. The paper sheets were placed between these pillars, in order to reduce the contact between sheets.

With a flow of 0.55 ml/min (using mass flow controllers), concentrated SO_2 was injected into the overall system. For concentrated NO_2 (N_2O_4) a flow of 1.1 ml/min was used. The first mixing was done with air (5500 ml/min). This stream of polluted air was partly taken to a mass flow controller, which leads to the pollution cabinet. The other part (excess of pollutants), was taken to a bypass and blown into a filter. Thus, approx. 500 ml/min polluted air was passed into the final mixing line of the cabinet. From the outlet, a pump was used to draw approx. 5000 ml/min polluted air out of the cabinet. The overall system was operated under atmospheric conditions. In the final mixing line, the 500 ml/min polluted air was mixed with 4500 ml/min pre-conditioned air at 23°C and 50% RH. The concentrations of the air pollutants were measured using a fluorescent SO_2 analyser, and a chemiluminescent NO_x analyser. The pollution cabinet with inner dimensions 526x486x425 mm was made of non-emitting materials, mainly PMMA (Plexiglas). Care was also taken to use non-emitting materials in seals, gaskets and tubing used to conduct air to and from the cabinet. This cabinet was placed inside the climate chamber, so that the temperature and relative humidity inside the cabinet could be controlled. The pollution cabinet had two separate inlets for the supply of the air pollutants and for the conditioned air, and eight outlets for polluted air. The equipment for the mass flow measurement and control consisted of a control and readout box and mass flow controllers. Temperature and relative humidity were monitored by placing a temperature and humidity sensor in the pollution cabinet. Gases were obtained in bottles delivered by AGA Gas B.V. The purities of the gases used were:

NO_2	99.0%
SO_2	99.98%

The concentrations of the air pollutants, $NO/NO_2/NO_x$ and SO_2, were monitored using analysers from API (Advanced Pollution Instruments). Both analysers covered the range from 0-30 ppm.

The experiments at CRCDG were also carried out using a Plexiglas cabinet. The homogeneity of circulation and concentration of pollutants was obtained with the help of a diffuser. The total air flow was low (2 to 6 l/min) in order to ensure a laminar flow along the samples and to ensure uniform conditions in the chamber. In contrast to the gases used at TNO, the gases were supplied in bottles of SO_2 and NO_x mixed with air at a concentration of 1%. The cabinet was placed in an oven in which the temperature was adjusted at 23°C. The humidifying system utilised the exchange of water vapour between flowing air and the surface of water in a sealed box. This system supplied air with a relative humidity of 100% that was then mixed with dry air. The desired relative humidity, 50%, was obtained by regulating the flows of dry and humid air with two mass flow controllers. The relative humidity and temperature were measured with an optical dew point controller. The SO_2 measurements were carried out with a UV fluorescence analyser for SO_2 and with a chemiluminescence analyser for NO_2 (Havermans 1992).

The results obtained from these experiments, were used only to calculate the relative deterioration rates.

Thermal ageing of the papers was performed separately using climate chambers in which the temperature and relative humidity could be set to and maintained at 90°C and 50% RH.

Chemical, physical and mechanical measurements were carried out to evaluate the behaviour of the materials used. A full description of the methods used is given in the annex of this thesis. In order to compare all the chemical results, the values calculated were corrected for the amount of water present in the samples after determining the amount of moisture (mc) according to TAPPI T 241 (TAPPI 1990).
The pH of the cold water extracts was measured to determine the acidity of the paper extracts (TAPPI 1988). The total organic compounds soluble in water (TOC) were determined according to Sprokholt, while the total amount of water-soluble ionic substances was found by measurement of the conductivity of the water extract (Skoog 1985; Sprokholt 1992). The TOC is calculated on the oven-dry weight of one gram of paper and expressed in ppm/g.
The copper number (Cu-No.) is a measure of reducing aldehydes and reactive keto groups and therefore the copper number provides an indication of the amount of oxidation/degradation which has occurred. In native cellulose, the only important reducing group is the terminal glucose unit of the long chain, and the copper number is very low. Oxidation and hydrolysis lead to an increased content of reducing, chiefly carbonyl groups. This was measured according to TAPPI T430 (TAPPI 1988). The average degree of polymerisation (DP_V) of cellulose was measured using the viscosity of a cellulose solution according to TAPPI T254 (TAPPI 1985). The alkali-extractable fraction (AEF) of the paper, is the amount of material that may be extracted by a 1% NaOH solution. The AEF contains mainly low molecular weight carbohydrate material and was measured according to TAPPI T 212 (TAPPI 1988). This fraction contains not only hemicelluloses, but also the degradation products and is expressed as a percentage of the weight of the oven-dry sample.

The mechanical properties of the paper samples were determined in the two principal directions, the machine direction (MD), and the cross machine direction (CD). From these values, the geometric mean of the property X was calculated according to $X_{gm} = \sqrt{X_{MD} \times X_{CD}}$.
The geometric mean value X_{gm} corresponds to an isotropic sheet, and its use facilitates the comparison of sheets with different mechanical anisotropies. Therefore, in most of the graphs, the geometric mean value is used. The term “index” is used in the paper industry to denote that a strength value has been normalised with respect to the grammage of the sheet. The tensile index, for example, is defined as the force (N) per unit width (m) per unit

grammage (g/m^2) that a strip of paper withstands at break. All tests were carried out at the standardised climate 50% RH and 23°C after the samples had been allowed to come to equilibrium in this climate. The two mechanical tests described in this section were the zero-span tensile strength, and the folding endurance according to Köhler-Molin (van Deventer, Havermans *et al.* 1994).

The zero-span tensile strength is dependent mainly on the fibre strength, and to only a minor degree on the bonding between the fibres. This test was therefore used to monitor the changes in the tensile strength of the fibre wall material, mainly the cellulose. The test was carried out using the Pulmac tester according to the TAPPI standard T 231 (TAPPI 1985). The folding endurance is determined by folding a strip of paper backwards and forwards through a specified angle, under a specified tensile load, until it breaks. The folding endurance is defined as the logarithm (base 10) of the number of double folds (SCAN 1977; ISO 1978). Folding endurance is the only fatigue test available in the field of paper physics.

5.4 Results and discussion

Firstly, the deterioration of the two types of cellulose will be discussed, followed by a discussion of the effects of acid and alkaline conditions in the paper. Finally, the relative rates of deterioration of the several materials used will be discussed. Because different experiments were carried out with similar materials, the schedule given in Figure 5.3 was used. Figure 5.3 also shows the abbreviations used. Measurements were therefore made after thermal ageing (aged), after artificial pollution (exp_t), and after the artificial pollution followed by a further period of thermal ageing (exp_t & aged).

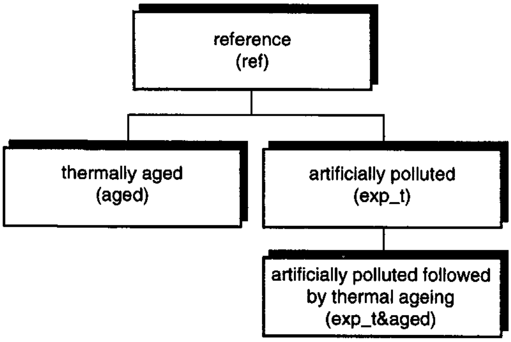


Figure 5.3 *The experimental schedule used*

5.4.1 Pure bleached softwood cellulose vs. pure cotton cellulose paper

Tests on paper-1, the one made of pure bleached sulphite softwood cellulose, and paper-2, the one made of pure cotton linters cellulose, showed that the initial DP_V of both these types of pure cellulose were similar (Figure 5.4). The chemical degradation of both celluloses can therefore be easily compared.

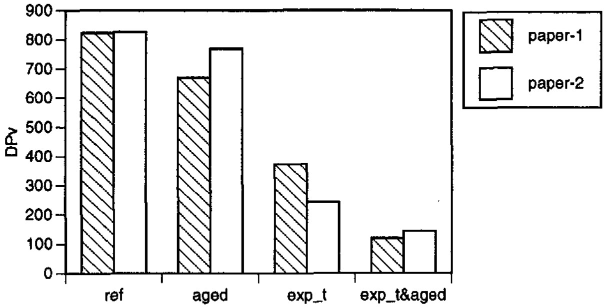


Figure 5.4 *Effect of thermal and pollutant treatment on the degree of polymerisation (DP_V) of paper-1, the bleached sulphite softwood cellulose paper, and paper-2, the pure cotton linters paper. Before (ref) and after thermal ageing (aged), after artificial SO_2, NO_x pollution TNO (exp_t), and after the artificial pollution followed by thermal ageing (exp_t&aged)*

It was found that the air pollutants substantially depolymerised the cellulose. This was especially true when the pollutant treatment was followed by thermal ageing. This combined effect was greater for paper-1 (bleached sulphite softwood cellulose), whereas after the pollutant treatment alone, paper-2 (pure cotton linters) was more deteriorated. Although the initial DP_V's of the two papers were comparable, their initial copper numbers and alkali-extractable fraction were different.

The copper number of paper-1 was lower than that of paper-2 (Figure 5.5), due mainly to the presence of the more extractable polysaccharides like hemicellulose that were present in paper-1. This fact was illustrated both by the size of the alkali-extractable fraction (Figure 5.6) and by infrared spectroscopy. The spectrum of the bleached sulphite softwood cellulose showed a specific band for hemicellulose at 815 cm^{-1}. This band was absent in the spectrum of the pure cotton linters (see also chapter 2).

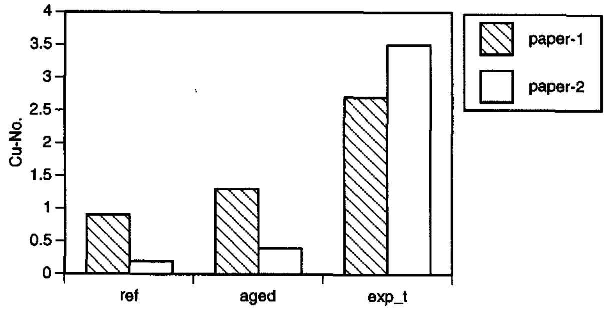


Figure 5.5 *Effect of thermal and pollutant treatment on the copper number of paper-1 (bleached sulphite softwood cellulose) and paper-2 (pure cotton linters). Before (ref) and after thermal ageing (aged), and after artificial pollution at TNO (exp_t)*

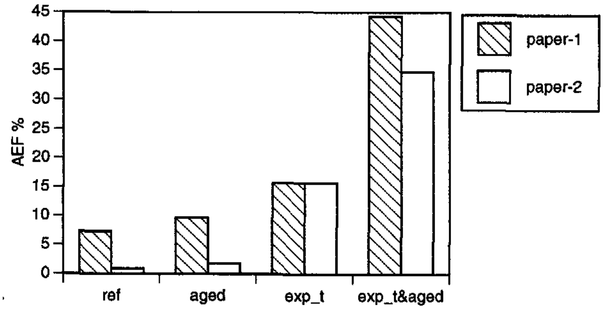


Figure 5.6 *Effect of thermal and pollutant treatment on the alkali-extractable fraction of paper-1 (bleached sulphite softwood cellulose) and paper-2 (pure cotton linters). Before (ref) and after thermal ageing (aged), after artificial pollution at TNO (exp_t), and after the artificial pollution followed by thermal ageing, (exp_t&aged)*

From these results, it can be concluded that thermal ageing for 12 days at 90°C and 50% RH, and 4 days exposure at 23°C and 50% RH to 20 ppm NO_x and 10 ppm SO_2 showed a similar pattern, in that both the copper number and the alkali-extractable fraction were increasing. These deterioration effects were however greater after exposure to NO_x and SO_2 then after this thermal ageing alone. Paper-1 showed a largerincrease in the copper number after the pollution, whereas the increase in the alkali-extractable fraction was greatest in paper-2.

The TOC data representing the non-dissociated small soluble organic compounds are shown in Figure 5.7. Again, paper-1 showed throughout a higher amount of TOC than paper-2. It can therefore be concluded that more end chain-cleavage occurs than chain-cleavage. Only at the thermal ageing after subjecting the materials to pollutants, we assumed that both cleavage reactions will occur.

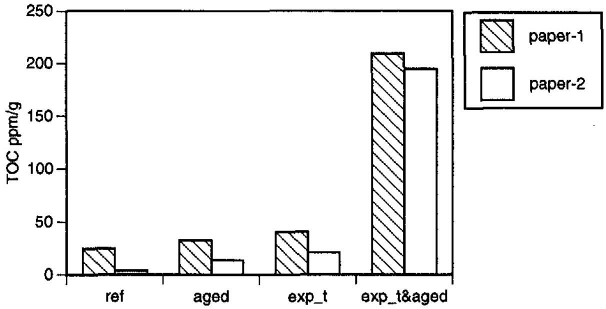


Figure 5.7 *Effect of thermal and pollutant treatment on the TOC of paper-1, the bleached sulphite softwood cellulose paper, and paper-2, pure cotton linters paper. Before (ref) and after thermal ageing (aged), after artificial pollution at TNO (exp_t) and after the artificial pollution followed by thermal ageing (exp_t&aged)*

The equilibrium moisture content decreased after each type of deterioration step (see Figure 5.8) indicating that the sorption capacity of the paper was reduced. This could be understood when the crystallinity of the cellulose structure was changed, and/or hornification had taken place.

Infrared spectroscopy showed that, due to the ageing, the crystallinity index (CI), see also section 2.3, of both types of cellulose did indeed increase (Figure 5.9). The increase was higher after the pollution step, which can be explained by a re-ordering of the cellulose chains (Iversen and Kolar 1991; Roberts 1991; Iversen 1992). Thus hornification did not take place (see also Chapters 3 and 4).

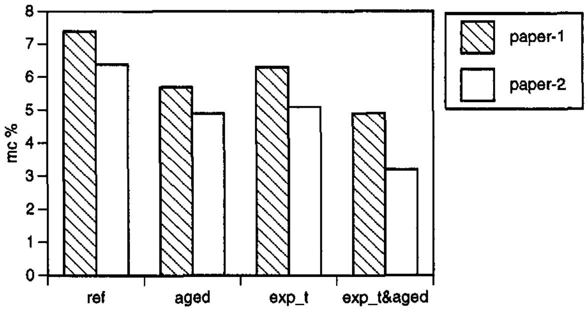


Figure 5.8 *Effect of thermal and pollutant treatment on the equilibrium moisture content (mc %) of paper-1, the bleached sulphite softwood cellulose paper, and paper-2, pure cotton linters paper. Before (ref) and after thermal ageing (aged), after artificial pollution at TNO (exp_t) and after the artificial pollution followed by thermal ageing (exp_t&aged)*

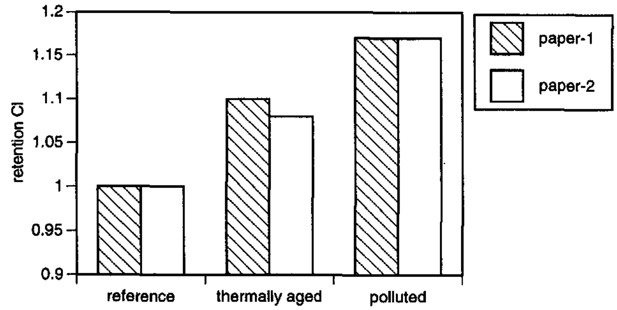


Figure 5.9 *Effect of thermal and pollutant treatment on the increase of the crystallinity index (CI), measured by infrared spectroscopy. The crystallinity index is a ratio of the intensities of the bands at 1372 cm^{-1} and 2900 cm^{-1}. The CI data in this graph are presented as retention values, i.e. all CI are divided by the reference CI; thus CI=1 means no change, CI>1 means an increase in CI*

In summary, 4 days exposure to 20 ppm NO_x and 10 ppm SO_2 at 23°C and 50% RH, causes more degradation in pure cellulose than thermal ageing for 12 days at 90°C and 50% RH.

Referring to the data obtained, we assumed that the type of deterioration mechanism mainly occurs in the presence of the air pollutants is a combination of acid-catalysed hydrolysis and re-ordering of the fibres. The main effect of thermal ageing exposing paper to the air pollutants alone is not a peeling-off of the glucose end group, but a chain-cleavage of the glycosidic bond. The thermal ageing after the artificial pollution results in a peeling of reaction also.

5.4.2 Alkaline paper *vs.* acid paper

Infrared spectroscopy revealed an interesting detail when alkaline papers were subjected to the SO_2/NO_x pollutants. Data for paper-5, an alkaline copy paper, showed that nitrates were formed as a result of the exposures. This was indicated by a sharp peak at 1378 cm^{-1} (see Figure 5.11). Furthermore, we found that the intensity of the peak increased in relation to the exposure time. At the same time, the calculated crystallinity index increased from 0.29 to 0.38. The nitrate band was found neither in the pure cellulose papers nor the acid paper used. This can indicate that alkaline papers are more sensitive to reaction with the air pollutants.The alkaline papers will form salts, especially when carbonates are used as fillers according to:

$$CaCO_3 + 2HNO_3 \rightarrow Ca(NO_3)_2 + CO_2 + H_2O \tag{3}$$

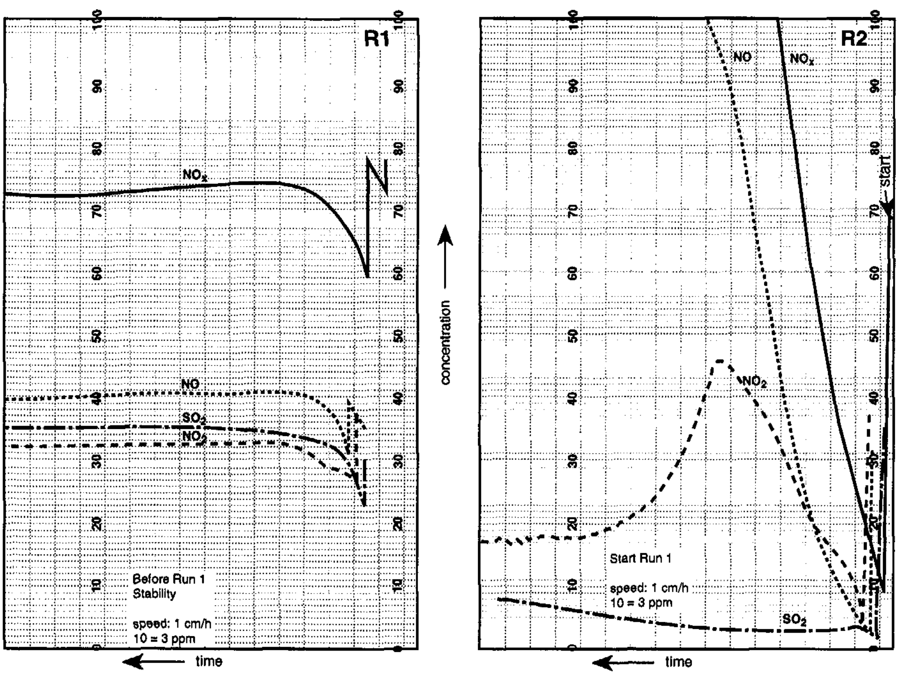
The experimental conditions may also lead to the formation of nitric and or nitrous acids. The nitrous acid may then decompose into nitric acid to give NO. During the registration of the concentrations of the different gases, we did indeed observe this effect: the concentration of NO increased during the experiments. This is illustrated in Figure 5.10. The pehnomena appeared to be completely reproducible.

In the presence of sulphur dioxide, the following reactions are therefore suggested to have taken place in the artificial pollution system with the formation of the unstable dinitrogen dioxide.

a) $$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2 \tag{4}$$

b) $$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O \tag{5}$$

c) $$2HNO_3 + SO_2 \rightarrow N_2O_4 + H_2SO_4 \tag{6}$$



(a) Stability check, before exposing the papers (b) Start exposing the papers

Figure 5.10 *The increase in the concentration of NO and NO_x in the effluent air, during exposure of the papers in the exposure cabinet. The x-axis is representing the exposure time recorded from right to left (1 cm/h), while the concentration of the air pollutants is given on the y-scale (10 units ≡ 3 ppm)*

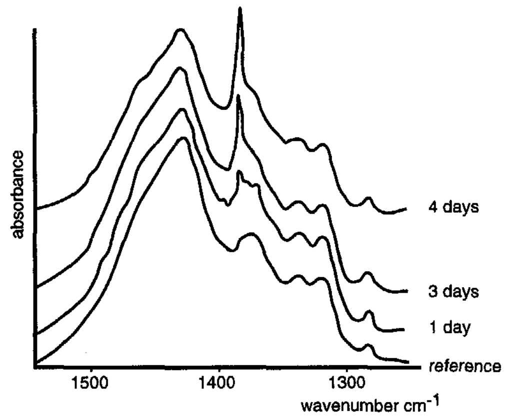


Figure 5.11 *Infrared spectra of paper-5 showing the increase in the peak at 1378 cm^{-1}. This peak indicates nitrates. The paper was sampled after 0, 1, 3 and 4 days exposure to an initial concentration of 20 ppm NO_x and 10 ppm SO_2 at 23 °C and 50% RH*

The zero-span tensile index generally reflects the strength of the constituent fibres (see also the annex). Figure 5.12 shows that this index decreased after each period of ageing or pollutant exposure especially in the case of the acid paper. Both paper-7, the acid copy paper, and paper-1, the pure bleached sulphite softwood cellulose paper, had lost much of their zero-span strength after the artificial pollution, while paper-5, the alkaline copy paper, remained relatively stable. The deterioration in the strength of the fibres in paper-7 was particularly extensive.

Figure 5.12 *Effect of thermal and pollutant treatment on the zero-span tensile index of three wood cellulose type papers: paper-1 (pure bleached sulphite softwood cellulose), paper-5 (alkaline and containing 50% softwood), and paper-7 (acid, and containing 40% softwood). Before (ref) and after thermal ageing (aged), after artificial pollution (exp_t) and after artificial pollution followed by thermal ageing (exp_t&aged)*

Figure 5.13 shows the calculated retention of the double folds. The retention was calculated as F_x/F_0, in which F_x is the measured number of double-folds after deterioration and F_0 is the measured number of double-folds of the unaged paper. It can be clearly seen that paper-7, the acid paper, and paper-1, the pure cellulose paper, had lost much of their fold-number after the artificial pollution, while paper-5, the alkaline copy paper, remained relatively strong. Paper-7 lost more than 50% of its strength already after the thermal ageing. When the paper was subjected to thermal ageing after the pollution step, only paper-5, the alkaline paper, retained some residual folding strength.

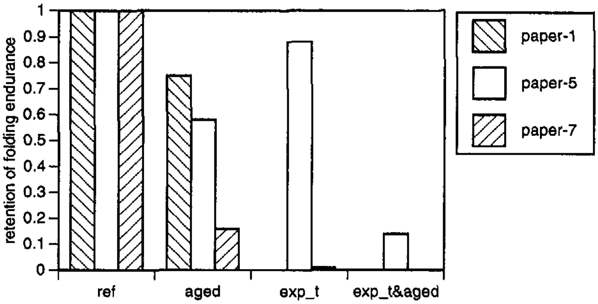


Figure 5.13 *Effect of thermal and pollutant treatment on the retention of fold number of the three wood cellulose papers before (ref) and after thermal ageing (aged), after artificial pollution (exp_t) and after artificial pollution followed by thermal ageing (exp_t&aged)*

The copper number showed a comparable increase in the case for paper-1 and paper-7, while the alkaline paper-5 was only slightly affected by the thermal ageing (Figure 5.14), indicating that alkaline compounds protect the fibres from acid contaminants but not from thermal ageing.

Figure 5.14 *The copper number of the three wood cellulose papers before (ref) and after thermal ageing (aged), and after artificial pollution (exp_t)*

The amount of degradation compounds formed after the different deterioration stages and represented by the alkali-extractable fraction, AEF (Figure 5.15), and the total organic compounds TOC (Figure 5.16), indicate that chain-cleavage took place during both thermal ageing and the exposure to pollutants. Again it was found that paper-5, the alkaline paper, deteriorated less than paper-7, the acid paper. After the thermal ageing, a decrease in the AEF was found, which might be due to some cross-linking effect. This observation deserves further study.

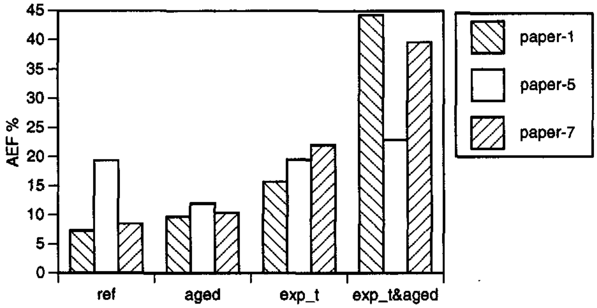


Figure 5.15 *Effect of thermal and pollutant treatment on the alkali-extractable fraction AEF of the three wood cellulose papers before (ref) and after thermal ageing (aged), after artificial pollution (exp_t) and after artificial pollution followed by ageing (exp_t&aged)*

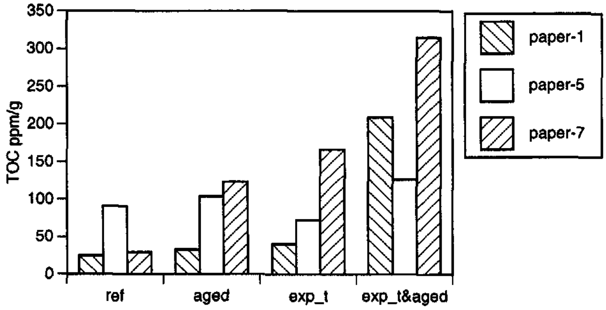


Figure 5.16 *Effect of thermal and pollutant treatment on the total organic compounds (TOC) of the three wood cellulose papers before (ref) and after thermal ageing (aged), after artificial pollution (exp_t) and after artificial pollution followed by ageing (exp_t&aged)*

In summary, the performance of the papers decreased more after the exposure to air pollutants than when subject to thermal ageing only. The presence of alkaline compounds in paper, such as calcium carbonate, promotes the absorption of the air pollutants with the formation of nitrates, thus reducing the acid-catalysed hydrolysis of the cellulose. Thermal ageing of alkaline paper showed a different deterioration pattern than the ageing due to the air pollutants SO_2 and NO_x. The deterioration is reduced less by the presence of calcium carbonate.

5.4.3 The relative deterioration rate

The relative deterioration rate can be defined as the rate of deterioration of the material being examined compared to that of a reference material. In this section, the bleached sulphite softwood paper was chosen as a reference, because almost all of the modern papers produced do contain (soft)wood cellulose. From the data for the alkali-extractable fraction (AEF) and the total extractable organic compounds (TOC), the relative deterioration rates were calculated for the papers used (see sectiuon 5.1). In contrast to previously discussed results, all available data were used to calculate the relative deterioration lines. As different raw materials were used for the papers, the comparison of the relative deterioration rate is presented according to paper composition.

Figure 5.17 shows the k·t-plot of the woodfree papers paper-5 and paper-7, the alkaline copy and acid copy respectively, against the k·t values for paper-1 as reference. It can be seen that the rate of deterioration of the woodfree paper-7 (acid copy) was higher than that of paper-5 (the alkaline copy). Furthermore, paper-7 showed a relative deterioration rate almost the same as that of the pure bleached softwood cellulose paper, paper-1. With regard to the absorption of the air pollutants, it was previously found that both papers, paper-1 and paper-7, were showing a similar absorption behaviour (Johansson and Lindqvist 1991).

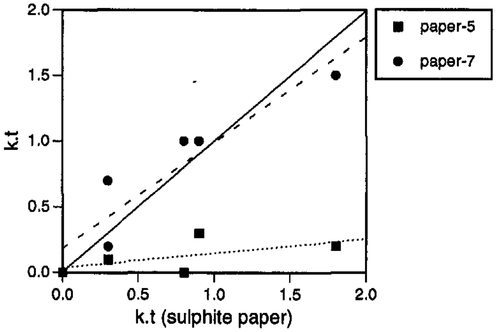


***Figure 5.17** A k·t-plot of two wood-free papers, paper-5 and paper-7, the alkaline and acid paper respectively, using the AEF-values. The acid copy paper is represented by circular symbols, while the alkaline paper is presented by square symbols. The thin solid line shows the 1:1 relationship with the reference paper-1, the bleached sulphite softwood paper*

Figure 5.18 shows the corresponding plot for the cotton-containing papers, paper-2, the cotton linters paper, and paper-4, the archival cotton paper. As given in Table 5.2, paper-4 contains approximately 4% calcium carbonate, which acts as a buffer against the acid attack. Again in this plot, it can be seen that paper-4, the alkaline cotton-containing paper, was less reactive than paper-2, the pure cotton linters paper.

Surprisingly, paper-2, the pure cotton linters paper, deteriorated more extensively than paper-1, the pure bleached sulphite softwood cellulose paper. It may be suggested, that the presence of hemicellulose in paper-1 acts as an internal resistor to slow down the deterioration of cellulose.

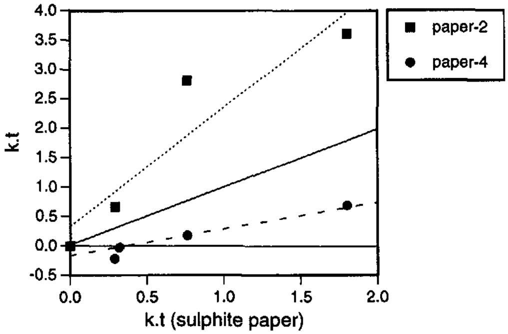


Figure 5.18 *A k·t-plot of two cotton papers, paper-2, the pure cotton linters one, and paper-4, the alkaline archival paper, using the AEF-values. The pure cotton paper is represented by square symbols, while the alkaline paper is presented by circular symbols. The thin solid line shows the 1:1 relationship with the reference paper-1, the bleached sulphite softwood paper*

Discussions continue concerning the behaviour of lignin-containing papers. It is a fact that lignin-containing papers yellow more rapidly than lignin-free papers, but their deterioration rates were not previously directly compared.

The deterioration of a mechanical pulp, *i.e.* a lignin-containing paper, may be seen in Figure 5.19. Here the k·t-values for paper-3, the acid mechanical paper and those of paper-7, the wood-free acid copy paper, are seen to be very similar to each other. The use of the different acid papers in this study, the lignin content obviously did not affect the deterioration rate.

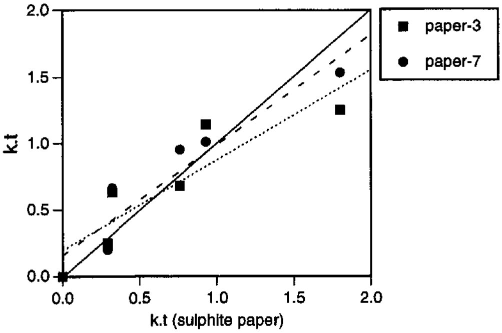


Figure 5.19 *A k·t-plot of two papers, an acid woodfree paper made of bleached softwood cellulose, and an acid wood-containing paper, the acid mechanical one, using the AEF-values. Paper-3, the wood-containing paper, is represented by square symbols, while paper-7, the woodfree paper, is presented by circular symbols. The thin solid line shows the 1:1 relationship with the reference paper-1, the bleached sulphite softwood paper*

Comparable results were found, using the TOC value, as a basis for the calculation of the relative deterioration rates as can be seen in Figure 5.20. The woodfree alkaline copy paper (paper-5) reacted more slowly than the woodfree acid copy paper (paper-7), while the wood-containing paper (paper-3) deteriorated at a rate similar to that of the pure bleached cellulose paper (paper-1). As the calculated line for paper-3 did not pass through the origin, it can be suggested that kinetics other than that of a first order hydrolysis plays a role in the deterioration. Therefore it is recommended that more specific research related to the kinetics of the deterioration be undertaken in the near future.

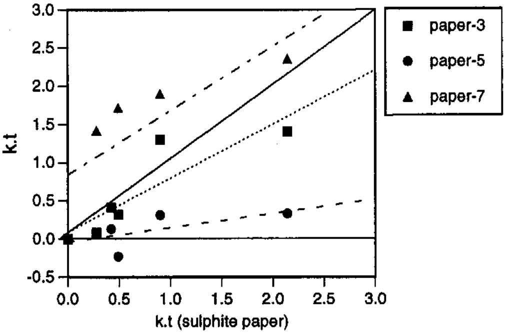


Figure 5.20 *A k·t-plot of paper-3, paper-5 and paper-7, an acid wood containing paper, an alkaline woodfree paper and an acid woodfree paper, using the TOC-values. The thin solid line shows the 1:1 relationship with the reference paper-1, the bleached sulphite softwood paper*

In summary, as expected for all the papers used, artificial pollution resulted in a drastic decrease in the pH, and an increase in the nitrate content in the alkaline papers. That inorganic products are formed was also shown in the case of the pure pulp materials in the absence of any additive by the increase in the conductivity of the cold-water extracts of the papers (Havermans, van Deventer *et al.* 1994). Thus a strong absorption of SO_2 and NO_x took place and, more importantly, the adsorbed gases reacted to form inorganic acids and or nitrates/sulphates when $CaCO_3$ was present in the paper.

The amount of degradation products found in the water extract, the TOC-value, depended not only on the artificial ageing process but also on the composition of the paper. The acid copy (paper-7) and the pure pulp materials (paper-1 and paper-2) showed the lowest initial TOC-values. Accelerated pollution of the papers resulted in two patterns. The TOC increased in the case of the pure pulp materials (paper-1 and paper-2), the acid copy (paper-7) and the acid mechanical paper (paper-3). The TOC-value decreased in the case of the alkaline paper (paper-5). Although the cotton linters paper showed the lowest TOC-value, the increase after ageing and pollution was one of the highest and was almost as large as paper-7, the acid (woodfree) copy paper.

After the different experiments it was also shown that, even if a sheet of paper was intact, the cellulose in the paper could be heavily deteriorated. Only the alkaline copy paper (paper-5) showed a substantial resistance towards cellulose degradation.

5.5 Conclusions

The following conclusions were drawn.

- The presence of 10 ppm SO_2 and 20 ppm NO_x for 4 days at 23°C and 50% RH caused a dramatic deterioration in papers without the presence of alkaline fillers. The air pollutants led to a faster deterioration of the paper than the thermal ageing processes used in *e.g.* standard test methods for determining paper durability.
- If NO_x is present, nitrates are formed only in alkaline papers. This indicates that the alkaline fillers in paper act as a protective agent towards acid attack by the air pollutants. This was furthermore supported by the relatively stable behaviour of the alkaline papers towards the air pollutants used.
- The deterioration of the cellulose in the presence of pollutants followed mainly an acid-catalysed hydrolysis, whereas during thermal ageing only (*i.e.* exposing for 12 days to 90°C and 50% RH) hydrolysis is combined with oxidation.

- Both deterioration processes resulted in a decrease in strength properties and in an irreversible loss of water sorption capacity of the papers used, while the crystallinity of the cellulose as measured by the CI increased.
- Chain-cleavage as well as reordering of the cellulose chains will take place in the presence of pollutants.
- Depending on the fillers and sizing in the paper, thermal ageing alone may cause cross-linking, and therefore reduce the formation of degradation compounds.
- Cotton showed a somewhat higher relative deterioration rate than bleached sulphite softwood cellulose. Both alkaline cotton and softwood cellulose-containing papers, showed a lower relative deterioration rate than the pure pulps.
- The lignin-containing paper used, showed a similar relative deterioration rate as the acid woodfree copy paper. Both rates were similar to that of the pure softwood cellulose. Lignin containing paper is thus not recommended for use in durable storage.

5.6 Recommendations

In order to obtain a more detailed insight in the ageing of cellulosic materials it is recommended to continue studies on the effects on its deterioration of alkaline compounds and of lignin in paper. In these studies, other relevant air pollutants (*e.g.* ozone, formaldehyde, acetic acid) should be included.

Acknowledgement

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References

Banik, G., W.K. Sobotka, A. Vendl and S. Norzcicsa (1993).
Effects of atmospheric pollutants on deacidified modern papers.
ICOM Committee for Conservation, Washington, II.

Birtwell, C., D.A. Clibbens and A. Geake (1926).
Journal of the Textile Institute 17: T145.

Browning, B.L. (1967).
Methods of Wood Chemistry.
New York, Wiley & Sons.

Daniel, F., F. Flieder and F. Leclerc (1990).
The effects of pollution on deacidified paper.
Restaurator 11: 179.

Daruwalla, E.H. and R.T. Shet (1962).
Heterogeneous Acid Hydrolyses of Alpha Cellulose from Sudanese Cotton.
Textile Research Journal 32: 942.

Deventer, J.P. van, J.B.G.A. Havermans and P. Kolseth (1994).
Materials. In: The influence of air pollutants on the accelerated ageing of cellulose containing materials.
STEP project CT 90-0100. Second Workshop, Paris, France.

Deventer, J.P. van, J.B.G.A. Havermans and P. Kolseth (1994).
Methods. In: The influence of air pollutants on the accelerated ageing of cellulose containing materials.
STEP project CT 90-0100. Second Workshop, Paris, France.

Havermans, J.B.G.A. (1990).
ACBAM Phase 5.1: Investigations on the accelerated ageing of paper under influence of sulfur dioxide.
PK 90.1008.
TNO, Delft, The Netherlands.

Havermans, J.B.G.A. (1992).
The experimental set up - Part 1. The Air-Pollutants. In: The influence of air pollutants on the accelerated ageing of cellulose containing materials.
STEP project CT 90-0100. Second Workshop, Paris, France.

Havermans, J.B.G.A. (1992).
The experimental set up - Part 2. The Equipment and Conditions. In: The influence of air pollutants on the accelerated ageing of cellulose containing materials. STEP project CT 90-0100. Second Workshop, Paris, France.

Havermans, J.B.G.A.; J.P. van Deventer; R. van Dongen; F. Flieder; F. Daniel; P. Kolseth; T. Iversen; H. Lennholm; O. Lindqvist; A.S. Johansson (1994).
The Effects of Air Pollutants on the Accelerated Ageing of Cellulose Containing Materials - Paper.
EC/DGXII/STEP project CT-90-0100, BU3.94/1068/JH.
TNO, Delft, The Netherlands.

ISO (1978).
ISO 5626; Paper - Determination of folding endurance.

Iversen, T. (1992).
Personal communication concerning the relaxation of cellulose molecules.

Iversen, T. and J. Kolar (1991).
Effects of nitrogen dioxide on paper.
FoU-projektet för Papperskonservering, Report No. 5.

Johansson, A.S. and O. Lindqvist (1991).
Effects of air pollutants on paper.
The deposition of SO_2 on paper: equipment and studies. In: The influences of air pollutants on the accelerated ageing of cellulose containing materials. STEP project CT 90-0100, First Workshop, Report PK 92.1027, TNO, Delft, The Netherlands.

Kimberly, A.E. (1932).
Deteriorative effect of sulfur dioxide upon paper in an atmosphere of constant humidity and temperature.
U.S. Bureau of Standards Journal of Research 8(February): 159.

Kolseth, P. (1992).
Accelerated Ageing of Paper - A Contribution to a Round Robin Test. In: The influences of air pollutants on the accelerated ageing of cellulose containing materials. STEP project CT 90-0100, First Workshop, Report PK 92.1027, TNO, Delft, The Netherlands.

Lyth Hudson, F. (1967).
Die Sorption von Schwefeldioxid durch Druckpapiere und deren chemische Beständigkeit.
Wochenblatt fur Papierfabrikation 95: 660.

Lyth Hudson, F., R.L. Grant and J.A. Hocke (1964).
The pick-up of sulfur dioxide by paper.
Journal of Applied Chemistry 14(October): 444.

Lyth Hudson, F. and W.D. Milner (1961).
Atmospheric sulphur and durability of paper.
Journal of the Society of Architectorial Historians 2: 166.

Martin, A.R., L. Smith, R.l. Whistler and M. Harris (1941).
Journal of Research of the National Bureau of Standards 27: 449.

Ott, E., Ed. (1943).
Cellulose and Cellulose Derivates. High Polymers.
New York, Interscience Publishers, Inc.

Priest, D.J. (1994).
Artificial ageing of paper: Correlation with natural ageing.
Workshop on the effects of aging on printing and writing papers, ASTM Headquarters, Philadelphia PA, ASTM Institute for Standard Research.

Roberts, G.A.F., Ed. (1991).
Accessibility of cellulose.
Paper Chemistry. London, Blackie.

SCAN (1977).
SCAN-P 17; Folding endurance. Köhler-Molin tester.

Skoog, D.A. (1985).
Principles of Instrumental Analysis.
Saunders College Publishing.

Springer, E.L. (1966).
Hydrolyses of aspenwood xylan with aqueous solutions of hydrochloric acid.
Tappi Journal 49: 102.

Sprokholt, R.P.A. (1992).
Het meten van de totale hoeveelheid opgelost en colloidaal organisch en anorganisch koolstof in de waterfase met behulp van de TOC-analyzer.
Centrum TNO Papier en Karton, Delft, The Netherlands.

TAPPI (1985).
TAPPI T 231; Zero-span breaking length of pulp.

TAPPI (1985).
TAPPI T 254; Cupriethylenediamine disperse viscosity of pulp (falling ball method).

TAPPI (1988).
TAPPI T 212; One percent sodium hydroxide solubility of wood and pulp.

TAPPI (1988).
TAPPI T 430; Copper number of pulp, paper, and paperboard.

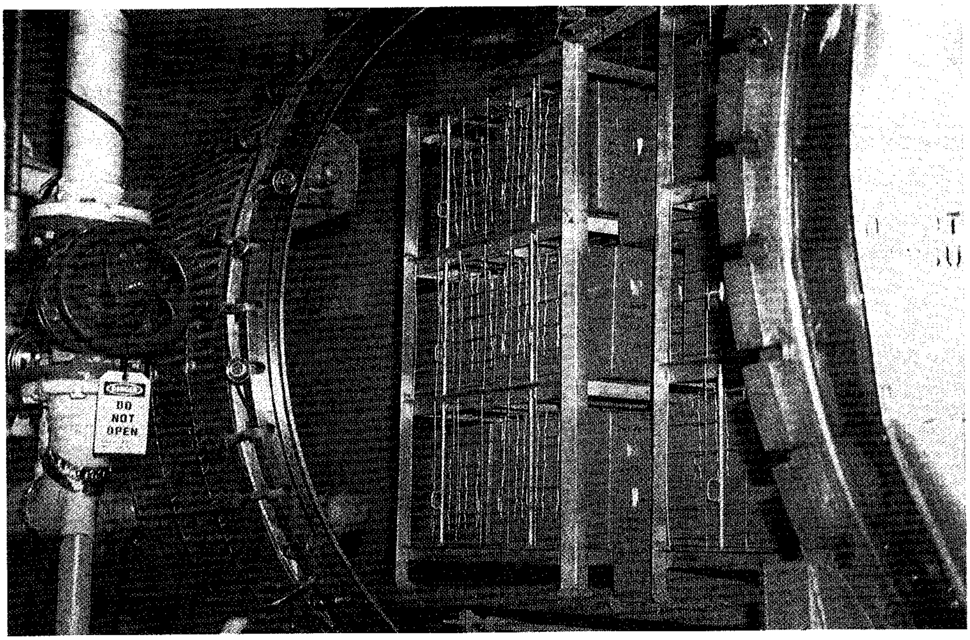
TAPPI (1988).
TAPPI T 509; Hydrogen ion concentration (pH) of paper extracts (cold extraction method).

TAPPI (1990).
TAPPI T 412; Moisture in paper and paperboard.

Young, A.R. and R.M. Rowell (1986).
Cellulose, Structure, Modification and Hydrolysis.
New York, John Wiley & Sons.

6

Mass Deacidification of Archival Materials using DEZ[*]



John B.G.A. Havermans[1], Ronald J.P. van Deventer[1], Ted A.G. Steemers[2]

1. TNO Centre for Paper and Board Research, Delft, The Netherlands
2. Dutch State Archives, The Hague, The Netherlands

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6. MASS DEACIDIFICATION OF ARCHIVAL MATERIALS USING DEZ

Summary

Mass Deacidification of Archival Materials using DiEthylZinc (DEZ)

The Dutch State Archives decided to use the DEZ-process for deacidification of a part of their collection consisting of 81 km of records dating from the period of 1840 to 1950, which are printed on acidic paper. TNO Centre for Paper and Board Research was commissioned to co-ordinate this programme. During the deacidification of 4 batches of the "Colonial Mail Rapport", reference test-materials were included in order to test the quality and reproducibility of the DEZ-deacidification treatment. It was shown that no pre-selection has to be made when only paper is inside the archival boxes. The reproducibility of the DEZ-treatment is good and an effective amount of alkaline compounds was introduced into the paper. No bad odour occurs after the treatment. After the treatment, the performance of the paper was slightly affected due to the change in the moisture content, but this should recover after an effective storage time.

It was concluded that a homogeneous deacidification occurred with the DEZ-process and that the treatment protects deacidified archive papers towards air pollutants like SO_2 and NO_x. The alkali-reserve can be seen as the most important factor for the protection of the paper against acid attack. The DEZ-process should be considered for application as a standard method for the deacidification of archival papers.

6.1 Introduction

One of the main causes of the deterioration of our paper-based cultural heritage is "acidification". The stored papers are becoming more and more acid, causing discoloration and deterioration of the paper. In some cases, the deterioration is so severe, that the stored documents can no longer be consulted: the paper breaks when touched. There are various causes of this acid degradation. One of the reasons is the paper-making process: an acid (sulphuric acid) or an acidic salt (alum) was added to the pulp in order to make the sizing agent (resin) effective. Another reason is the uptake of acid-producing contaminants present in the ambient air in which the materials are stored.

Because paper is still one of the main carriers of information it is of extremely importance, that our paper-based cultural heritage can be used and consulted for much longer than our own lifetime. The cultural heritage of the past is now the seed of our scientific and cultural activities. Therefore papers have to be preserved for the future. Considering the amount of paper stored in the major archives and libraries (approximately 25,000 km of records equivalent to 1 billion books), manual-deacidification methods can no longer in a short time protect these materials. Therefore mass treatment is necessary. There is also an economical reason, the costs for mass-deacidification treatments are lower than that of manual deacidification. For example DEZ-treatment of 1 m paper will cost approximately *f* 700,- while the costs for manual-treatment of 1 m paper can be upto *f* 3000,- (Miller 1993).

There were also some of the main conclusions of a study performed as a commission of the Dutch National Preservation Office, C.N.C. (Hol and Voogt 1991). The need for mass-deacidification of their 19th and 20th century archives induced the Dutch State Archives to take a closer look at available mass-deacidification systems. A preliminary desk-research was performed by the Dutch National Preservation Office (Neevel 1991), which arrived at the conclusion that deacidification of archival materials with a gas-diffusion process is to be preferred over liquid-diffusion processes.

During the last 15 years, many mass-conservation methods were developed aiming at stopping the deterioration of paper. One of these methods was the treatment of paper with DiEthylZinc (DEZ) gas (U.S.Congress 1988). This three step diffusion process, drying-diffusion-rehydration, not only neutralises the acids in the paper, but also forms an alkaline buffer in the paper for preventive purposes (Miller 1993).

In 1993, a detailed experimental study concerning the application of the DEZ-deacidification for archival and newsletter materials by TNO (Havermans and van Deventer 1993; van Deventer and Havermans 1993) was finished. It was concluded that the alkali-reserve after the treatment was homogeneous and that the general performance of the materials used was good after the treatment. Scanning electron microscopy (SEM) showed a homogeneous distribution of the zinc oxide particles around the fibres. MacInnes and Barron (1992) drew the same conclusions concerning the uniformity of the deposition of the ZnO using the same techniques (Barron 1993). Also after exposure of the deacidified papers to a thermal ageing process, the deacidified papers deteriorated more slowly than the non-deacidified papers. Roelofs *et al.* (1992) found also comparable results, while Pauk and Porck (1994) concluded that the treatment of library materials with DEZ has disadvantages. They agreed that in libraries these disadvantages play a more important role than in archives.

Havermans and van Deventer (1993) concluded, that the packaging of the materials to be deacidified has to be improved. The use of closed archive boxes was the main reason why papers stored in the boxes located in the middle of the deacidification room showed a high emission of volatile carbon compounds like butanol and other alcohols. Another important study was on the different types of crystals, *e.g.* $ZnSO_4$, which could be formed after a DEZ-treatment and after the uptake of, for example, sulphur dioxide (Schoute 1993). From this case study it was concluded that the type of crystals formed after the DEZ-treatment and the type of crystals which could form after reacting with sulphur dioxide will not contribute to the deterioration of the paper.

After these studies and after contacting several Institutions in the United States of America, who already contracted AKZO for treatment (Barron 1993; Harris 1993), the Dutch State Archives decided to use the DEZ-process for deacidification of a part of their collection. This part comprises 81 km of records on acidic paper dating from the period of 1840 to 1950, which is at risk, because after a damage survey it was concluded, that already 1.5% of the overall collection was brittle and unusable. In close co-operation with TNO Centre for Paper and Board Research, the State Archives started their deacidification programme on original archival material. Although previous research proved that no pre-selection was necessary for a deacidification treatment, this viewpoint had to be reconsidered for the following archival reasons:

- According to the results of the inventory damage survey (Hol and Voogt 1991), the materials to be deacidified have to be from the 19th century, and preferably from the period between 1870 and 1879.
- The information has to exist in another format. In this case it was also available on microfilm.

- The archives have to be in the category of substitutable archives. This means that, after putting the information on another format, the originals are allowed to be destroyed. This, however, will be only possible when the new Archive Act in the Netherlands has been approved and published (foreseen in 1995).

It was important that the State Archives made this kind of pre-selection, because the materials had to be shipped to the United States by air-freight. The risk of losing originals during transport or treatment was therefore substantial. Considering these reasons the Dutch State Archives has chosen the "Colonial Mail Rapport" for deacidification.

During the deacidification of four batches of the "Colonial Mail Rapport", reference test-materials were included to testing the quality, efficiency and reproducibility of the DEZ-deacidification treatment, because it was not allowed to carry out any test on the original materials.

This chapter describes the results and conclusions concerning the **deacidified reference test-materials** and the stability of these deacidified materials against acid contamination.

6.2 Deacidification with DEZ, principles and practise

The DEZ process is based on gas diffusion. DEZ molecules penetrate between the leaves in an archives case or between the pages of closed books. The process treatment is the result of a 20 year development history and its origin was practised for the first time by chemists of the Library of Congress Preservation Research and Testing Office in Washington DC, USA. Nowadays, papers which were treated at that time, enjoy a very good shape (Harris 1993).

The process was licensed to AKZO Chemicals Inc. and performed at the plant located at Deer Park, Houston, Texas (Miller 1993).

The principle of the deacidification and other reactions of DEZ can be summarised as follows:

DEZ reacts very rapidly with the organic as well as the inorganic compounds present in paper *e.g.* hydroxyl groups and carboxylic groups of cellulose, the residual moist present in the paper, and the sulphuric acid formed due to hydrolyses of the alum sulphate present in the paper.

The main reactions which will take place during the deacidification are:

Reaction with the hydroxyl groups of cellulose (cell)

$$2R_{cell}\,COH + (C_2H_5)_2Zn\,(g) \rightarrow (R_{cell}CO)_2Zn\,(s) + 2\,C_2H_6\,(g) \qquad (1)$$

Reaction with the carboxylic groups of cellulose

$$2R_{cell}COOH + (C_2H_5)_2Zn\,(g) \rightarrow (R_{cell}COO)_2Zn\,(s) + 2\,C_2H_6\,(g) \qquad (2)$$

Mixed reaction with the hydroxyl groups and carboxylic groups of cellulose

$$R_{cell}COOH + R_{cell}\,COH + (C_2H_5)_2Zn\,(g) \rightarrow$$

$$(R_{cell}CO)(R_{cell}COO)Zn\,(s) + 2\,C_2H_6\,(g) \qquad (3)$$

Reaction with sulphuric acid

$$H_2SO_4 + (C_2H_5)_2Zn\,(g) \rightarrow ZnSO_4\,(s) + 2\,C_2H_6\,(g) \qquad (4)$$

The zinc sulphate formed remains in the paper, while the ethane gas is removed.

Reactions with water

$$H_2O + (C_2H_5)_2Zn\,(g) \rightarrow ZnO\,(s) + 2\,C_2H_6(g) \qquad (5)$$

$$ZnO\,(s) + H_2O \rightarrow Zn(OH)_2 \qquad (6)$$

Because the paper to be deacidified is predried *i.e.* the moisture content of the paper is lower than 0.5%, it is to be expected that most of the excess of DEZ will initially form ZnO, which will remain in the paper as an alkali-reserve. The solubility of ZnO in water is 1.6 mg/l (25°C), and the pH of the water extracts of the treated paper will be therefore approximately 7.5. ZnO is amphoteric, dissolving in acids to form salts and in alkalis to form zincates, such as $[Zn(OH)_3]^-$ and $[Zn(OH)_4]^{2-}$. ZnO can also react with alkaline compounds. Therefore the pH of the extract of the treated paper can never exceed the value of 9.5 according the following reaction:

$$ZnO + 2\,OH^- + H_2O \rightarrow [Zn(OH)_4]^{2-} \qquad (7)$$

The remaining ZnO protects the paper against the acid-catalysed hydrolysis of the cellulose.

The mechanism of ZnO dissolution (hydroxylation) has been discussed by several authors and varied from a dissociative one (Savvin, Gutman *et al.* 1981) to a redox one (Sengupta, Ahluwalia *et al.* 1975; Sengupta, Ahluwalia *et al.* 1979) obviously water adsorption onto ZnO will start with hydroxylation of the ZnO.

$$(ZnO)_n + H_2O \rightleftarrows \text{-ZnOH-O-ZnOH-} \tag{8}$$

Reaction with oxygen

One of the disadvantages of the use of DEZ it the violent exothermic reaction with oxygen according to

$$7\,O_2 + (C_2H_5)_2Zn\,(g) \rightarrow ZnO\,(s) + 4\,CO_2 + 5\,H_2O \tag{9}$$

The treatment therefore is to be carried out in an inert atmosphere.

The whole DEZ-treatment, a three-stage process carried out on our paper materials, is summarised below:

Drying

The first stage of the process is drying. Warm dry nitrogen is flushed through the deacification chamber and this dries the paper and consequently leads to an increase in the amount of water in the vapour phase. Using vacuum and a so-called "cold finger", the water in the vapour phase is removed. The final water content of the paper after the drying stage is lower than 0.5% by weight. The drying is actually a multistage process on its own. In general, four heating and cooling stages were performed from 35°C to a maximum of 54°C. During heating, the pressure is changed from 1000 to 0.65 torr. After the drying phase, liquid nitrogen is flushed through the system in order to make the environment inert.

Diffusion

During the diffusion step, solvent-less DEZ is introduced into the deacidification chamber to deacidify the papers using nitrogen gas as a carrier. The pressure was approximately 15 torr while the temperature increased from approximately 21°C to 54°C. After the permeation step is completed, excess of DEZ is removed by purging with nitrogen while the temperature is decreased to approximately 15°C. The initially amount of DEZ introduced, was approximately 8.2 kg.

Rehydration

Rehydration is the final stage in the whole process. Moisture is injected into the deacidification chamber at approximately 54°C to increase the moisture content of the deacidified materials before the deacidification chamber is opened. After this stage, a 3-day humidification at 50% RH is carried out.

6.3 Materials, methods and logistics

The test materials used were a bleached sulphite softwood paper (code paper-1) and an acid mechanical pulp paper (code paper-3), see also Chapter 5, Table 5.2. The first paper (initial pH = 6.7) contained no additives, fillers or sizing agents. The second paper was made of groundwood-containing pulp and was alum-rosin sized (initial pH = 5.9). Both papers had a grammage of 80 g/m^2. The materials were wrapped in archival boxes and stored in different locations in the whole batch of original archives, which was prepared by the Dutch State Archives for the deacidification. The container with the materials was sent to Houston, Texas for the deacidification treatment. At Houston, the containers were kept unopened until the start of the treatment. The archival boxes containing the archival materials and the test materials were placed on a special developed rack in the deacidification chamber without any repackaging of the materials. The lid of each archival box was previously removed by the Dutch State Archives. During transport, the temperature and relative humidity in the container were recorded continuously by remote control sensors.

Directly the materials had been returned to The Netherlands, the boxes with the test materials were transported to the research lab of TNO Delft, where they were stored in the dark at 23°C and 50% relative humidity. Table 5.1 shows the dates of the different DEZ-treatments.

Table 5.1 *The 5 treatments*

Treatment code	Date of treatment
Run - 0 (Pre-run)	October 1992
Run - 1	June 1993
Run - 2	September 1993
Run - 3	October 1993
Run - 4	February 1994

The deacidified materials were investigated with respect to visual changes in the materials including microscopic research and illumination under UV-light for possible deformations and salt-deposition on the paper. Photoexcitation will occur by photons with an energy equal to or greater than the band gap energy (312 kJ), and will raise the electrons from the electron-filled valence band to the conduction band. An almost filled valence band behaves like a filled band with positive electron carriers called holes. The excitation process can be seen by holding a sheet of paper, treated with DEZ, under a UV lamp. The homogeneity of the distribution of the alkaline compounds was examined by measuring the zinc content using Atomic Absorption Spectroscopy (AAS) and the alkali-reserve (ASTM D 4988) of the papersheets.

Deacidified specimens and their references were subjected to thermal ageing by storing the papers for 12 days at 90°C and 50% RH. In one of the series, deacidified paper and its reference paper also exposed for 4 days against air pollution using concentrations of NO_x = 20 ppm and SO_2 = 10 ppm at a climate of 23°C and 50% RH. These artificial pollution conditions were similar to the conditions as used in the European Research EC/DGXII/STEP CT90-0100 project (Havermans *et al.* 1994). In these experiments, 98 sheets of one type of paper (size A4) were placed vertically in a Plexiglas exposure cabinet. The air flow containing the air pollutants was introduced into this chamber through a perforated wall. The concentrations of air pollutants were continuously measured by SO_2 and NO_x analysers (see also Chapter 5).

Before and after the accelerated ageing and artificial pollution, analyses were performed. The pH of the cold water extract of the paper according to NEN 2151 shows not only the alkalinity of the deacidified papers, but it also indicates that absorption of pollutants and formation of acid compounds occurred during the artificial pollution experiments (NEN 1981). The pH was determined using 0.1 M NaCl to examine the alkaline compounds inside the fibres (Scallan 1990). Deterioration products which can be formed after an artificial deterioration experiment were examined using the alkali-extractable fraction according to ASTM D 4988 (ASTM 1992). The equilibrium moisture content shows the morphological changes in the paper before and after each treatment (TAPPI 1990). The mechanical performance of the paper was examined by measuring the tear resistance (NEN 1989) and folding endurance (Köhler Molin) of the papers (ISO 1978). On additional samples, scanning electron microscopy with X-ray analyses (SEM/EDXA) was carried out to look at the homogeneity of the distribution of the alkaline zinc compound on the fibres. Before and after the artificial pollution, two extra chemical tests were carried out. Firstly the copper number (Cu-No.) indicating the content of reducing groups in the paper, was measured (TAPPI T 430), and secondly the degree of polymerisation (DPv) of the cellulose present in the paper was determined according to TAPPI T 254 (TAPPI 1985; TAPPI

1988). Here the measured viscosity is related to the average chain length or molecular weight of the cellulose.

The samples and their abbreviations can be summarised using the schedule below. If a run number is necessary for further interpretation of the results, the code will be followed by the run number for example: paper-1 treated in the second deacidification run is coded as *1D2*.

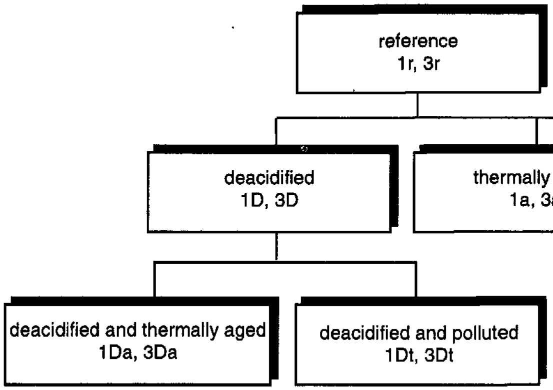


Figure 6.1 *Sampling and testing schedule including the abbreviations used for the corresponding papers (treated and untreated)*

6.4 Results and discussion

6.4.1 The homogeneity of the deacidified papers

The homogeneity of the distribution of the ZnO was first visually determined using an UV-lamp (582 nm) and is shown in Figure 6.2a.

Secondly the distribution of Zn in the paper was examined using atomic absorption spectroscopy. Both investigations showed that the distribution of the ZnO was homogeneous. An exception was RUN 2, in which case a larger amount of Zn-compounds was introduced into the paper. This can be seen in Figure 6.2b, where the Zn-content in the sheets is given. The graph also shows the difference between the middle and the margin of a sheet. The margin of a papersheet is here defined as a cut strip of 5 cm around a papersheet while the middle is defined as the remaining part of the papersheet, after removing the strip of paper from the margin.

It was also shown that the acid mechanical paper (paper-3) contained more Zn than the softwood sulphite cellulose paper (paper-1). This can be attributed to the fact that the acid mechanical paper is more acid (average initial pH = 5.9) than the softwood sulphite cellulose paper (average initial pH = 6.7).

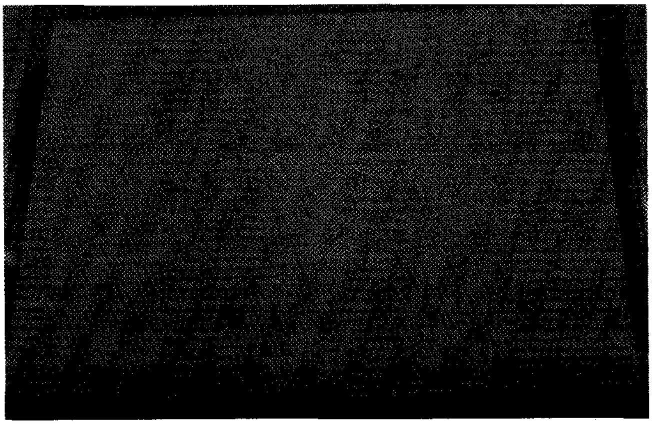


Figure 6.2a *Photograph of the distribution of Zn in the paper determined using an UV-lamp (582 nm)*

Figure 6.2b *The Zn content of the deacidified sheets in mg Zn per gram ovendry paper*

6.4.2 Chemical analyses

It was found that the measured pH value of the cold water extract from the deacidified sheets was independent of the location of the sheet in the archive box. The average pH (from the margins and middles of these sheets) is shown in Figure 6.3 for the acid mechanical paper (*paper-3*) only. Comparable results were obtained with the softwood sulphite cellulose paper (*paper-1*). A slight decrease in the pH value after the thermal ageing treatment was found for the untreated papers (reference) only. No significant difference in the pH value was found among the four DEZ-treatments. This was shown using the t-test (p=0.05). Thermal ageing alone did not influence the acidity of the deacidified papers.

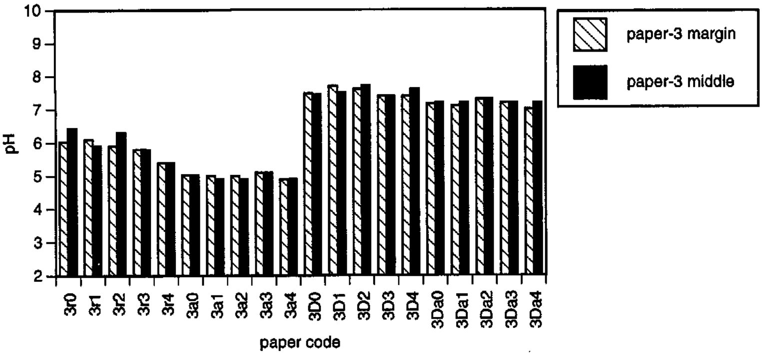


Figure 6.3 *The pH of the cold water extract of the margins and middles of sheets from the acid mechanical paper (paper-3), before and after the deacidification, and after the thermal ageing. The paper code is according to Figure 6.1, for example, 3D1 = paper-3, DEZ treatment, run 1*

The pH of the extract using a 0.1 M NaCl solution to measure the pH inside the fibre wall of the papersheets, showed an even more homogeneous distribution. No significant differences were found between the different runs. The average for paper-1 is shown in Figure 6.4. After deacidification, the pH of both paper extracts was 7.2, which was slightly decreased after the thermal ageing.

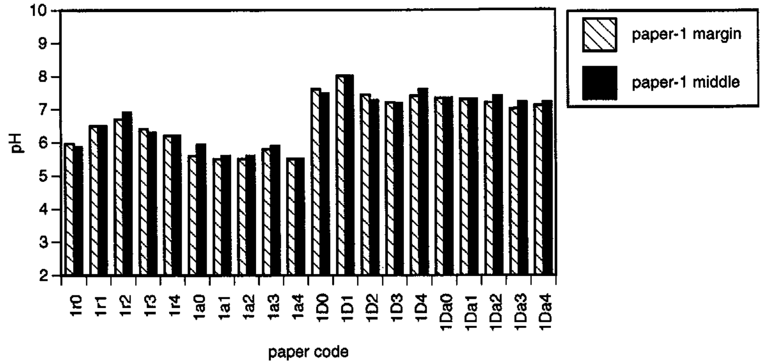


Figure 6.4 *The pH of the cold water extract of paper-1 using 0.1 M NaCl solution, before and after the deacidification and after the thermal ageing. The paper code is according to Figure 6.1, for example, 1D3 = paper-1, DEZ treated, run 3*

The data for the alkali-reserve show that all the DEZ-treated papers were given an alkali reserve of about 0.3 - 0.4 mol/kg. With the exception of the first DEZ-run (RUN 0), no influence of the location of the sheet the sheet in the archive box was found in the measured alkali-reserve. There was a difference between the acid mechanical and sulphite cellulose paper, the alkali-reserve for the acid mechanical paper being about 0.1 mol/kg higher. The averages of the alkali-reserve in mol/kg of the sulphite cellulose paper are shown in Figure 6.5. It can also be seen from this Figure that, upon the thermal ageing alkaline compounds are consumed possibly due to the formation of deterioration products, like carboxylic acids, in the paper. However, after the accelerated ageing an effective amount of alkali-reserve still remained.

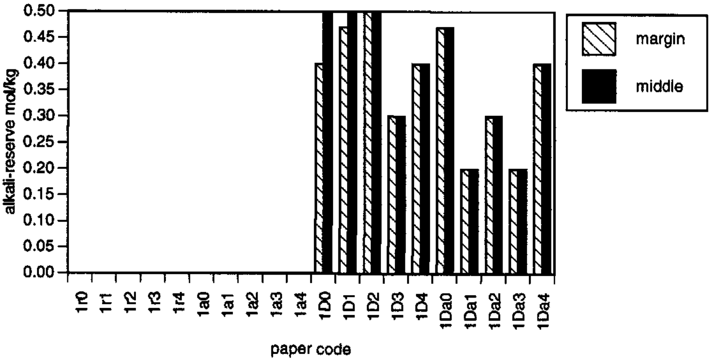


Figure 6.5 *The alkali-reserve of paper-1, before and after deacidification and after thermal ageing. The paper code is according to Figure 6.1, for example, 1D3 = paper-1, DEZ treatment, run 3*

The alkali-extractable fraction, AEF (see also Figures 6.6 and 7.6), represents the amount of extractable poly- and oligosaccharides that is soluble in a 1% alkali solution and is therefore an indication of the amount of deterioration products formed, the higher the AEF the higher is the amount of degradation. Since no significant difference was found between the AEF of the reference and that of the deacidified papers, it can be concluded that the deacidification treatment does not affect the materials. The results obtained from RUN 0 and 4 show that the AEF increased after the deacidified papers had been aged in an accelerated way (see Figure 6.6). So a slight deterioration effect occurred due to exposures to high temperature and humidity.

The differences in the total amount of extractable compounds between the acid mechanical and sulphite softwood cellulose papers are due to the use of different raw materials. Groundwood-containing papers always contain more extractables than the woodfree papers.

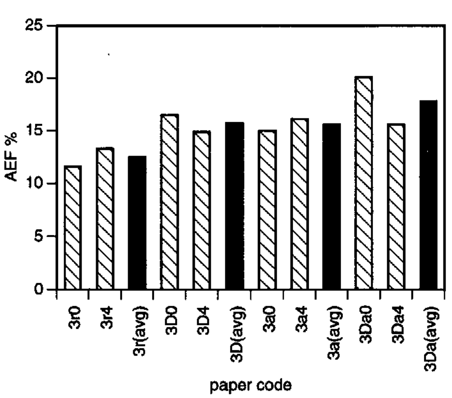


Figure 6.6 *The alkali-extractable fraction as a percentage of the oven-dry paper-3 before and after deacidification and after thermal ageing. The average of the alkali-extractable fractions is also given (avg). The paper code is according to Figure 6.1, for example, 3D0 = paper-3, DEZ treatment, run 0*

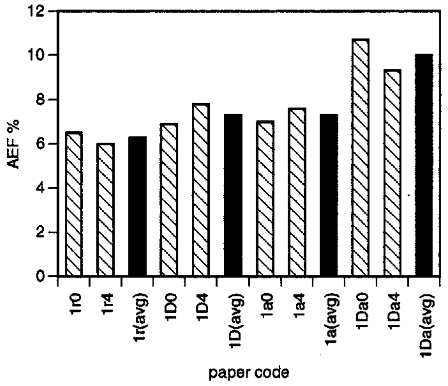


Figure 6.7 *The alkali-extractable fraction as a percentage of the oven-dry paper-1 before and after deacidification and after thermal ageing. The average of the alkali-extractable fractions is also given (avg). The paper code is according to Figure 6.1, for example, 1D4 = paper-1, DEZ treatment, run 4*

6.4.3 Mechanical analyses

Since chemical properties cannot represent the behaviour of the paper during normal use, two types of mechanical analyses were performed, the tensile strength and the folding endurance. From the results obtained, the retention values, *i.e.* the value of the actual value divided by its reference value, were calculated. In Figures 6.8 and 6.9 these values are presented for the tensile strength in the machine direction of the acid mechanical paper and the softwood sulphite cellulose paper, respectively.

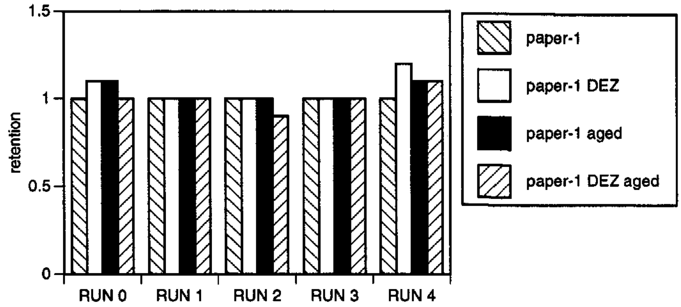


Figure 6.8 *The tensile strength retention of paper-1 represented by the ratio of the measured tensile strength in the machine direction before and after deacidification and after thermal ageing*

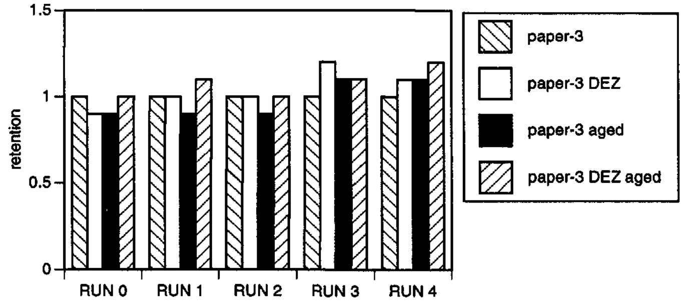


Figure 6.9 *The tensile strength retention of paper-3 represented by the ratio of the measured tensile strength in the machine direction before and after deacidification and after thermal ageing*

It is clear in both Figures 6.8 and 6.9, that the DEZ-treatment does not cause any decrease in the tensile strength of the acid mechanical paper (paper-3), except for RUN 0. In some cases, the tensile strength even increases slightly. After the thermal ageing, there was in most of the cases no significant decrease or increase of the tensile strength of the DEZ-treated papers. For the bleached sulphite softwood-cellulose paper (paper-1) better results were even obtained; only in RUN 2 there was a decrease in the tensile strength of the deacidified paper after accelerated ageing.

The folding endurance of the papers defined as the logarithm of the amount of double folds showed a somewhat different picture as can be seen in Figure 6.9, where the logarithm of the double folds is presented from paper-1. After the DEZ-treatment no significant decrease in the folding endurance was found, but after the thermal ageing the folding endurance decreased in all cases. For RUN 2, the decrease was even significantly higher than for the untreated paper. This effect may be attributed to the fact, that there is a predrying stage within the whole process. The equilibrium moisture content of the deacidified paper was therefore decreased and not totally recovered when the tests were performed. For example the moisture content of the paper-1 decreased after the deacidification from 7% to 5.5% and was not recovered before running the mechanical tests.

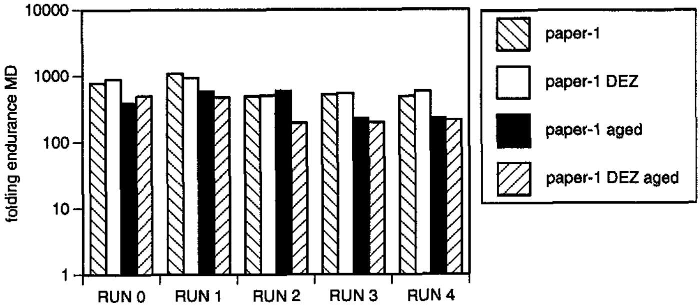


Figure 6.10 *The folding endurance of paper-1 before and after deacidification and after thermal ageing*

6.4.4 Stability towards air pollutants

After 4 h of artificial exposure towards 20 ppm NO_x and 10 ppm SO_2 at 23°C and 50% RH, the pH of both the exposed paper-1 and paper-2 decreased substantially, but much less than in the case of the nontreated papers, as can be seen in Figure 6.11. It should be noted that the pH of the DEZ-deacidified papers (paper-1 DEZ and paper-3 DEZ) was higher than the initial reference value. This reflects the protective work of the alkaline compounds.

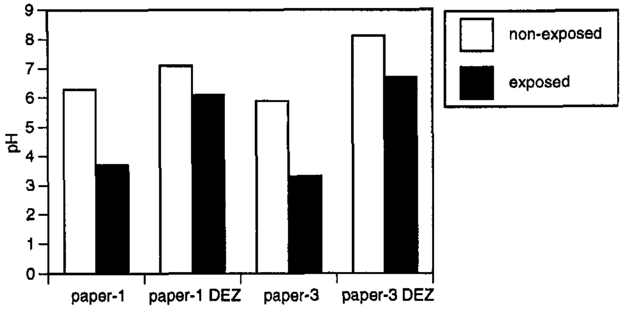


Figure 6.11 *The pH of the cold water extract of the reference and deacidified papers before and after the exposure to air pollutants (4 days at 20 ppm NO_x and 10 ppm SO_2 and at 23°C and 50% relative humidity)*

To gain more insight in the observed degradation due to air pollutants, the alkali-extractable fraction, the degree of polymerisation and the copper number were determined. Polymers with a degree of polymerisation (DPv), higher that about 300 are measured by the method applied and represented by their DPv. The reducing properties of the paper were examined by the copper number (Cu-No.). The copper number indicates the presence of reducing aldehydes and reactive keto groups and therefore the copper number indicates the amount of degradation.

The papers exposed to air pollutants showed a decrease in the DPv and the AEF, and an increase in the Cu-No. indicating a substantial deterioration took place caused by acid-catalysed hydrolysis and by oxidation. The protective function of the DEZ-treatment is demonstrated by the DPv of paper-1 (Figure 6.12). After the artificial pollution, it was found that the DEZ-treated paper degraded much less than the untreated paper. Combining this result with the Cu-No. data, is was evident that the cellulose chains in the reference papers were not only cut into smaller pieces, but also that more reducing aldehydes and reactive keto groups were formed. The primary alcohol groups of the cellulose at the C6 position are possibly involved. It was again found that the amount of reducing groups of the exposed DEZ-treated sulphite softwood cellulose paper was comparable to that of its untreated reference material, whereas in the case of the acid mechanical paper, the increase in reducing groups was less in the DEZ-treated paper than in the untreated paper (see also Figure 6.13).

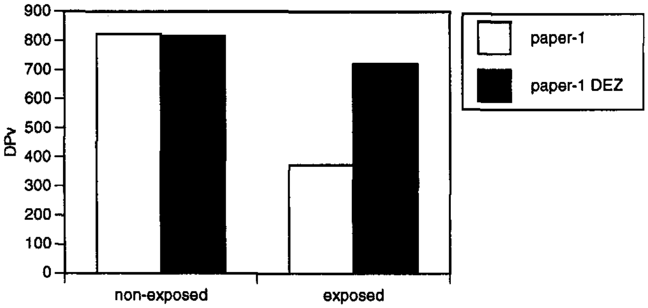


Figure 6.12 The DPv of the reference and deacidified paper-1 before and after the exposure to air pollutants (4 days at 20 ppm NO_2 and 10 ppm SO_2 and at 23°C and 50% relative humidity)

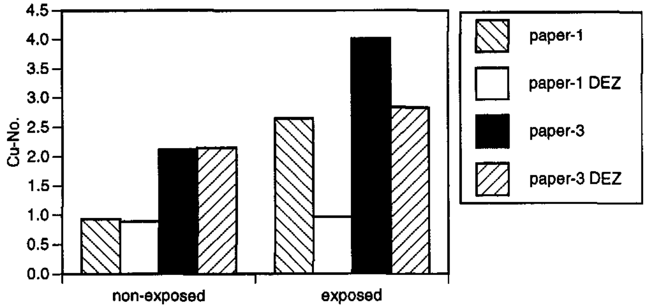


Figure 6.13 *The Cu-No. of the reference and deacidified papers-1 and -3 before and after the exposure to air pollutants (4 days at 20 ppm* NO_2 *and 10 ppm* SO_2 *and at 23°C and 50% relative humidity)*

Using the AEF, the effect of lowering the deterioration can be shown. Here the approach was made, that the deterioration followed first order reaction kinetics (Daruwalla and Shet 1962; Springer 1966). To calculate the relative deterioration rates, $k{\cdot}t$ (see Chapter 5) the following formula was used:

$$\ln\left[\frac{P_t}{P_0}\right] = k \cdot t \tag{1}$$

Here $[P_0]$ is the AEF at t=0 or the AEF of the reference $[P_r]$, and $[P_t]$ is the AEF after each deterioration experiment. The calculated relative deterioration rates *($k{\cdot}t$)* for each paper are projected on the y-axis in Figure 6.14, while on the x-axis only the *($k{\cdot}t$)* values of the bleached sulphite softwood-cellulose, paper-1, (internal standard) are projected. An increase in the relative deterioration rate results in an increase in the angle with the x-axis. Figure 6.14 shows, that the deterioration rate was reduced for the DEZ-treated papers, paper-1 DEZ and paper-3 DEZ, the angle with the x-axis for the DEZ-treated paper decreased compared to that of the untreated papers.

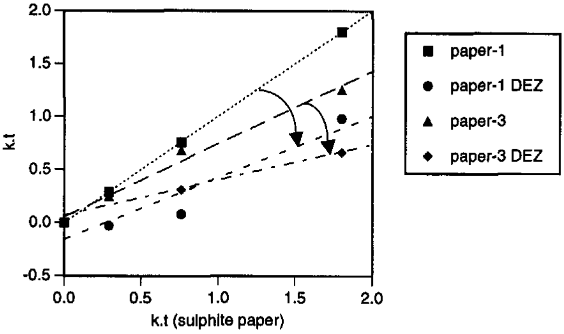


Figure 6.14 *The calculated relative deterioration rates (kt) of the softwood sulphite and acid mechanical reference (paper-1 and paper-3) and of the DEZ-deacidified papers (paper-1 DEZ and paper-3 DEZ)*

6.5 Conclusions

It can be concluded not only that a homogeneous deacidification occurred with the DEZ-process but also that the treatment is indeed very effective when archive papers are subsequently exposed to air pollutants. Except for archival reasons, no pre-selection has to be made, when only paper is inside the archival boxes. The package of each archival box is apparently to be considered as not too tight.

It was also shown that the reproducibility of the DEZ-treatment is excellent and that, in all cases, an effective amount of alkaline compounds was introduced into the paper. The amount of zinc introduced was not representative of the homogeneity because, during the treatment, DEZ reacts with the acid compounds present and turns them into alkaline compounds. It was proven, that the measured pH value of the cold water extract alone does not stand for an effective treatment, but that the alkali reserve does, and this can be seen as the most important factor for the protection of the paper against acid attack. The performance of the paper can be slightly affected, when the papers are treated with DEZ due to the change in the equilibrium moisture content, but after an effective time the moisture content of the deacidified paper will be recovered.

Finally it should be considered to standardise the DEZ-process for the deacidification of archival papers, although AKZO Chemicals Inc. decided to close the DEZ-plant at DeerPark, Houston, Texas. The author expresses the hope that funds will be found for setting up a new plant for the preservation of our cultural heritage.

Acknowledgement

The financial assistance of the Dutch State Archives, Den Haag, The Netherlands, is greatly appreciated. Discussions with prof. Andrew Barron, dr. Mildred Jeffery and dr. Petter Kolseth were beneficial. AKZO at Dear Park, Houson is greatfully acknowledged for their kind hospitality during our visit at the DEZ-plant.

References

ASTM (1992).
ASTM D 4988; Determination of alkalinity of paper as calcium carbonate (alkaline reserve of paper).

Barron, A. (1993).
Personal Communication about DEZ.
Harvard University, Cambridge, Boston.

Daruwalla, E.H. and R.T. Shet (1962).
Heterogeneous Acid Hydrolysis of Alpha Cellulose from Sudanese Cotton.
Textile Research Journal 32: 942.

Deventer, J.P. van and J.B.G.A. Havermans (1993).
Effectiviteit DEZ-proces. Evaluatie met ingebonden Nederlandse kranten. PK 93.2001.
TNO, Delft, The Netherlands.

Harris, K. (1993).
Personal Communication about research on DEZ.
Washington D.C., USA.

Havermans, J.B.G.A. (1992).
The experimental set up - Part 2. The Equipment and Conditions. In: The influence of air pollutants on the accelerated ageing of cellulose containing materials. STEP project CT 90-0100. Second Workshop, Paris, France.

Havermans, J.B.G.A.; J.P. van Deventer; R. van Dongen; F. Flieder; F. Daniel; P. Kolseth; T. Iversen; H. Lennholm; O. Lindqvist; A.S. Johansson (1994).
The Effects of Air Pollutants on the Accelerated Ageing of Cellulose Containing Materials - Paper. EC/DGXII/STEP project CT-90-0100, BU3.94/1068/JH.
TNO, Delft, The Netherlands.

Havermans, J.B.G.A. and J.P. van Deventer (1993).
Voorstudie DEZ. Het ontzuren van twee referentiepapieren. PK 93.2001.
TNO, Delft, The Netherlands.

Hol, R.C. and L. Voogt (1991).
Endangered Books and Documents.
CNC publications 2.
CNC, The Hague, The Netherlands.

ISO (1978).
ISO 5626; Paper - Determination of folding endurance.

Miller, R. (1993).
The deterioration of modern records and books, and the DEZ vapor phase process. AKZO, Deer Park, Houston.

Neevel, J.G. (1991).
Methoden voor Massaconservering.
Analyse en evaluatie.
NCN Publications 1.
CNC, The Hague, The Netherlands.

NEN (1981).
NEN 2151; Bepaling van de pH van een waterige suspensie.

NEN (1989).
NEN 2013; Bepaling van de treksterkte-eigenschappen.
Methode met eenparige treksnelheid.

Pauk, S., H. Porck (1994).
Pilot research into the effects of the Battelle and Diethylzinc mass deacidification methods.
CNC Publications 8.
CNC, The Hague, The Netherlands.

Roelofs, W.G.Th., J.H. Hofenk de Graaff, R. van den Meulen, M. Knoppe, P.B. Hallebeek (1994)
Onderzoek naar het effect van Di-ethylzink ontzuren op de veroudering van papier.
Centraal Laboratorium voor Onderzoek van Voorwerpern van Kunst en Wetenschap Amsterdam, Project 92/242.

Savvin, N.N., E.E. Gutman and I.A. Myasnikow (1981).
Nature of absorption ventres of atoms and molecules of oxygen on metallic oxides in relation to electrical conductivity and infrared spectroscopic data.
Russian Journal of Physical Chemistry 55: 498.

Scallan, A.M., Ed. (1990).
The pH inside the Fibre Wall. In: Cellulose and Exploitation: Industrial Utilization, Biotechnology and Physico-Chemical Properties.
London, Ellis Howard.

Schoute, M.F.E. (1993).
Kristallen in ontzuurd papier.
Chemiewinkel, Laboratorium voor kristallografie, Universiteit van Amsterdam.

Sengupta, G., H.S. Ahluwalia and S.P. Sen (1975).
Zinc oxide - water vapour system. Mechanism of adsorption from electrical conductivity studies.
Journal of Catalyses 36: 111.

Sengupta, G., H.S. Ahluwalia, S.P. Sen and B. Banerjee (1979).
Chemisorption of water vapour on zinc oxide.
Journal of Colloids & International Science 69: 217.

Springer, E.L. (1966).
Hydrolysis of aspenwood xylan with aqueous solutions of hydrochloric acid.
Tappi Journal 49: 102.

TAPPI (1985).
TAPPI T 254; Cupriethylenediamine disperse viscosity of pulp (falling ball method).

TAPPI (1988).
TAPPI T 430; Copper number of pulp, paper, and paperboard.

TAPPI (1990).
TAPPI T 412; Moisture in paper and paperboard.

U.S.Congress (1988).
Book Preservation Technologies.
Office of Technology Assesment, Washington D.C.

ANNEX 1

Terms and abbreviations used

Term or abbreviation	Explanation
ACBAM	An abbreviation for 'onderzoek naar de mate van Aantasting van Cellulose- en ligninehoudende materialen in relatie tot de concentratie van luchtverontreinigende verbindingen in Nederlandse Bibliotheken, Archieven en Musea' (Dutch research program on the deterioration of cellulose- and lignin containing materials caused by air pollutants).
Acid paper	Paper manufactured with a pH below 7.0.
AEF	Alkali-extractable fraction.
Ageing	A general term describing the natural degradation of paper, adhesives and other archival materials, while in storage.
Air pollutants	Substances present in the air that pollute the environment
Alkali-extractable fraction	The amount of organic compounds dissolving in alkali.
Alkaline paper	Paper produced with alkaline chemistry and having a pH of 7.5 or greater.
Alkali-reserve	The quantity of alkaline substance present in the paper and capable of counteracting the formation of acids in paper.
Alum	Aluminium sulphate hydrate ($Al_2(SO_4)_3.xH_2O$).
Artificial ageing	Subjecting paper to a process which increases the rate of deterioration.
Artificial pollution	Subjecting paper to a process which increases the rate of deterioration by exposing the paper to high levels of air pollutants.
ASTM	American Society for Testing and Materials.
ATR	Attenuated Total Reflectance.
Auto-oxidation (Autoxidation)	A self sustaining decomposition of a chemical compound (here cellulose) caused by oxygen and/or oxygen radicals.
Bleaching process	An oxidising or reducing process that removes residual lignin and increases the brightness of the pulp.
Brightness	A measure of the lightness/whiteness *etc.* Specifically for paper the reflectance factor weighed according to a function which has a maximum value at 457 nm and a band width at half height of 44 nm.

Term or abbreviation	**Explanation**
C.N.C.	Coordinatiepunt Nationaal Conserveringsbeleid (Dutch National Preservation Office).
Coating	Term applied to the layer of adhesive mixture of a clay or calcium carbonate pigment, or mixture of pigments, applied to the surface of paper to provide a smoother base for printing.
Copper number	A measure of the reducing groups in cellulose, *i.e.* groups that can be oxidised easily. In native cellulose, for example, the only reducing group is the terminal glucose unit of the cellulose chain.
CRCDG	Centre de Recherches sur la Conservation des Document Graphiques.
Cross-machine direction	The direction perpendicular to the direction in which a machine-made paper travels through a papermaking machine.
Crystallinity index	A measure of the extent of crystallinity of the cellulose.
CTMP	Chemithermomechanical pulp.
D_2O	Deuterium oxide.
Deacidification	The addition of alkaline compounds to acid paper to neutralise paper.
Depleted ageing	Artificial deterioration using an oxygen-depleted environment.
Deterioration	Heading towards a worse condition.
DEZ	Diethylzinc.
Diethylzinc	A volatile organometallic compound ($Zn(C_2H_5)_2$) used both to neutralise paper and to create an alkali reserve in paper by adding zinc oxide deposits.
Digitised information	Information stored in different form on, for example, digital audiotape, hard disc.
DPv	Degree of polymerisation (DP), measured as the intrinsic viscosity (v), of a solution of cellulose dissolved in *e.g.* cupriethylenediamine.
DRIFT	Diffuse Reflectance Infrared Fourier Transform .
Fibrillation	Bruising and roughening of the fibre walls during the beating process in pulp refining in order to create more surfaces for fibre to fibre bonding during sheet formation.
FTIR	Fourier Transform Infrared.

Term or abbreviation	Explanation
Grammage	The weight of paper expressed in grams per square meter.
Groundwood pulp	Stone groundwood or refiner mechanical pulp or thermomechanical pulp, woodpulp containing a great deal of lignin.
Hardwood cellulose	Cellulose obtained from hardwoods.
Hemicellulose	Fraction of polysaccharides in wood, consisting of low molecular weight glucans, *e.g.* xylans and glucomannans.
Hornification	An irreversible loss of swelling capacity that follows for example upon extensive drying or heating of cellulosic materials.
Hydrogen bonds	A type of bond formed when a hydrogen atom bonded to atom P in one molecule makes an additional bond to molecule Q either in the same or another molecule.
Hydrolysis	Decomposition or splitting into other compounds by taking up the elements of water.
Inert ageing	Artificial deterioration using an inert environment.
IR	Infrared.
IRE	Internal Reflection Element.
ISO	International Organisation for Standardisation.
Isotropic sheet	Sheet of paper without any cross-machine or machine direction.
Kaolin	A whitish earthy material composed primarily of the clay mineral, kaolinite, and used in a refined form as a filler in papermaking, coating components and opacifying agent.
Kraft cellulose	Cellulose produced by a modified sulphate process, using only wood pulp. "Kraft" is a Swedish word meaning "strong".
KRS-5	A synthetic mixed-crystal thallium bromide iodide, approximately 42:58 Br:I. Highly toxic.
k/s	Kubelka-Munk unit.
k·t-value	Relative deterioration rate.
Kubelka-Munk unit	k/s, where k is the absorption coefficient and s the scattering coefficient, both depending on the particle size and refractive index of the sample to be investigated and on the wavelength of the light.
Kubelka-Munk formula	$\frac{(1-(S/R))^2}{2\cdot S/R}=\frac{k}{s}$ where S is the reflectance of the sample and R the reflectance of the reference.

Term or abbreviation	Explanation
Lignin	A three dimensional amorphous polymer of phenyl propane units, with a variable structure so complex that a definitive formula for it can not be given.
Machine direction	The direction in which paper travels through a papermaking machine. The fibres tend to some extent to be preferentially oriented in this direction.
mc	Moisture content.
MCT detector	Mercury Cadmium Telluride detector.
Microfilm	High resolution film used to record micro-images.
Microwave radiation	Electromagnetic radiation.
Moisture content	(Weight of sample minus weight of dried sample) divided by the weight of sample in %.
N_2O_4	Dinitrogen dioxide.
NEN	Nederlandse Norm, Dutch standardized method published by “het Nederlands Normalisatie Instituut”, NNI, Delft.
NO_x	Oxides of nitrogen, here the sum of the concentrations of NO and NO_2.
Optical brightener	A chemical compound making the paper look brighter due to fluorescence.
Paper	A fibrous mat produced by a filtration process in which a dilute slurry of fibres in water is caused to flow across a screen, allowing the water to drain out. Paper derives its name from papyrus.
Papyrus	A tall sedge (Cyperus papyrus) native to the Nile region, the pith of which was sliced into longitudinal strips and pressed into matted sheets. The forerunner of paper.
PAS	Photo Acoustic Spectroscopy.
Permanent paper	Paper that should last at least for several hundred years without significant deterioration under normal library use and storage conditions.
pH	Negative logarithm to base of 10 of the hydrogen ion concentration. The letters pH stand for pouvoir hydrogène or “hydrogen power”.
PMMA	Polymethylmethacrylate (plexiglas).

Term or abbreviation	Explanation
ppm	Parts per million.
Pulp	The mechanically and/or chemically prepared fibrous mixture used in the manufacture of paper and board.
Relative deterioration rate	Rate of a certain deterioration reaction, not direct related to the time.
Relative humidity	The ratio expressed as a percentage, of the amount of water vapour actually present in the air to the greatest amount of vapour the air could hold at that temperature.
Response time	The time to reach a steady state.
Retention values	Values obtained by dividing the actual value by its original value.
RH	Relative humidity.
Rosin	The residue obtained after distilling off the volatile matter (turpentine) from the gum of the southern pine.
Rosin size	A solution or dispersion obtained by treating rosin with a suitable alkali. When properly converted in the papermaking process, usually by the addition of alum, the size precipitates and imparts water resistance to paper.
SEM	Scanning electron microscopy.
Size	An additive that makes the fibre surface of paper hydrophobic and keeps the paper from acting like blotting paper when written or printed upon. Early papermakers dipped their handmade sheets into vats of gelatine in order to size them.
Softwood cellulose	Cellulose obtained from softwood.
STEP	Science and Technology for Environmental Protection.
Sulphate process	Pulping of woodcellulose by removing the wood components as lignin and hemicellulose using alkaline chemicals.
Sulphite process	Pulping of woodcellulose under removing the woodcomponents as lignin and hemicellulose using acid chemicals.
Tensile strength	The property of paper that enables it to resist breaking under tension.
TGS detector	Triglycine sulphate pyroelectric detector.
Thermal ageing	Ageing using dry heat or combined high temperature and high humidity.

Term or abbreviation	Explanation
TMP	Thermomechanical pulp.
TNO	Nederlandse organisatie voor Toegepast Natuurwetenschappelijk Onderzoek.
TOC	Total Organic Carbon.
Total Organic Compounds	The fraction of organic compounds which is soluble in water related to the TOC measure.
Viscosity	The viscosity is related to the chain length or molecular weight of the cellulose.
Watermarks	An image or symbol formed in a sheet of paper during its manufacture which is visible when the paper is held up to transmitted light.
Woodfree paper	A misleading word. Woodfree paper does not contain recognisable lignin-containing wood particles, although the source of the cellulose is mostly of wood.

ANNEX 2

Methods used

Contents

Spectroscopic & Microscopic Techniques

1. Atomic Absorption

Atomic Absorption Spectroscopy (AAS) is used to determine the amount of cation deposited by deacidification treatment (Mg, Zn, Ca) or the filler content of paper. With the atomic absorption spectrometer, the absorbance of the radiation emitted by a hollow cathode lamp is measured. Another application using AAS is to determine metallic impurities in the paper (Cu, Fe,...) which can accelerate the degradation of cellulose by catalysis of hydrolytic reactions. The tests are made according to TAPPI T 266 (TAPPI 1988b).

The samples are taken from different parts of the paper sheet (margin, centre, corner). Approximately 1 cm^2 of paper is ignited in a silica crucible placed in a oven at (575±25)°C for 3 hours. The ash is then dissolved in 5 ml of HCl and diluted with an aqueous solution of 15 wt% $LaCl_3$.

The method is calibrated with solutions of known concentrations (0.1 to 5 ppm). These solutions contain about 5% of HCl and 15% of $LaCl_3$.

For example, the conditions to determine the magnesium content are:
- wavelength: 285.2 nm,
- slit width: 0.5 nm,
- type of flame: air–acetylene.

Other relevant compounds are calcium and zinc (*cf.* DEZ-process).

2. Fourier Transform Infrared Spectroscopy (FTIR)

The infrared spectrum of a paper provides a distinctive and permanent record that constitutes a "fingerprint" based on the components present. Although the spectra are often difficult to interpret owing to the complex composition of paper, they may aid in establishing the similarity of two specimens and in characterising the composition to trace the source of a single specimen.

Different chemical components in the paper sample, *i.e.* crystalline cellulose, lignin, hemicellulose, etc., as well as fillers and other relevant compounds can be quantitatively determined (see for example: Havermans 1991; Willis *et al.* 1987).

The substance is prepared as a pellet by pressing at high pressure the pulverised sample mixed with an infrared-transparent material. Potassium bromide is commonly used. The pellet is usually about 13 mm in diameter, and contains approximately 1 mg of sample and 300 mg KBr.

The samples are prepared with a sharp knife edge (scalpel) and some fibres are scratched from the sample.

The FTIR instruments, software and other specifications used at TNO, Delft, are listed in table A2.1.

Table A2.1 *FTIR system used at TNO*

Apparatus		Application/parameters
BRUKER 113v FTIR	Detector	TGS or Nitrogen-cooled MCT
	Range	4000–400 cm^{-1} (25 mm–2.5 mm)
	Resolution	1-2 cm^{-1}
	Pressure	Vacuum
	No. of scans	64 in transmittance 250 in reflectance
SPECTRA-TECH IR-PLAN analytical microscope Coupled to a BOMEN MB100 FTIR.	Magnification	187x
		15x, binocular 10x
	Objective	internal magn. 1,25x
	Detector	Nitrogen-cooled narrow band MCT
	Range	4000–750 cm^{-1} (13 mm–2,5 mm)
	Resolution	2-4 cm^{-1}
	Pressure	Atmospheric
	No. of scans	approx. 100
SPECTRA-CALC™ software Galactic Industries Corporation (version 2.1)	Applications:	DATA-acquisition BOMEN MB100 FTIR DATA-manipulation DATA-operating

3. Light microscopy for fibre analysis

Microscopic methods are essential when magnification is necessary in the examination of form and structure (Browning 1977). Fibre analysis of paper is performed under a microscope. TAPPI standard T 401 (TAPPI 1988c) describes the procedure for the identification of different kinds of fibres.

The sample of paper is cut into fragments and placed in a sodium carbonate solution (5%). This mixture is boiled for 10 minutes and is then filtered to remove the fillers and sizing and rinsed with water. The fibres are separated in a mixer or a test tube strongly shaken after the addition of a few drops of acetic acid. The sample is sifted out and rinsed again. A small amount of the pulp obtained is humidified and defibrillated on a microscope slide with a needle, and two coloured reagents are added: zinc chloroiodure (Herzberg reagent) and Lofton Merrit reagent. The colours of the fibres after this treatment indicate the treatment of the pulp (Lofton Merrit) or the nature of the fibres (Herzberg) as shown in Table A2.2. The form and size of the elements permit recognition of the vegetal origin of the fibre.

Composition of the reagents

Herzberg reagent

Solution A : $ZnCl_2$ 20 g (pure and dried), water 10 g,
Solution B : I_2 0.1 g, KI 2 g, water 5g.
The two solutions are mixed and left standing until clear (12–24 h).

Lofton Meritt reagent

Rosaniline or Fuchsine base 0.22 g; malachite green 0.22 g; HCl conc. 1 ml; water 500 ml. The colorants are dissolved in a few ml of water and all the compounds are then mixed together.

Table A2.2 *The colours of the fibres*

Sample	Herzberg	Lofton Meritt
Mechanical pulp	yellow	blue green
Chemical pulp (*unbleached*)		
Kraft	blue violet	blue green
Sulphite	blue violet	violet
Bleached chemical pulp	blue violet	uncoloured
Cotton (pure chiffon)	red	uncoloured

4. SEM/EDXA

Scanning electron microscopy/electron dispersive X-ray analysis (SEM/EDXA) is used to reveal fibre or sheet structure and to make a qualitative elemental analysis for the determination of the kind of filler in the paper.

The sample (about 1 cm^2 of paper) is not electrically conductive, so it is coated by evaporation and deposition at low pressure of a 5 to 10 nm layer of metal (gold or palladium) or carbon.

The range of useful magnification is 5 to 30 000. In the SEM/EDXA, interaction of incident electrons with bound electrons in atoms of the sample gives rise to X-ray photons. An X-ray detector permits the identification of elements with an atomic number of 11 (sodium) or greater.

Quantitative analysis can be carried out by the use of standards and reference materials. Elemental analysis can be performed in either micro and macroregions. Elemental mapping is possible to show the distribution of an element over the surface of the specimen.

Chemical analysis

1. Alkali-extractable fraction

This method is used to determine the alkali-extractable fraction (AEF) of the paper (TAPPI 1988a).

The paper sample (approx. 2 g) is extracted with a hot 1% sodium hydroxide solution. The hot alkali solution extracts the low molecular carbohydrates, consisting mainly of hemicellulose and degraded cellulose.

The amount of alkali-extracted carbohydrates is related to the degradation of the cellulose.

The percentage of alkali-extracted carbohydrates is calculated as the weight residue divided by the weight of the sample.

$$\text{AEF}\ (\%) = \frac{A-B}{A} \cdot 100 \qquad (1)$$

Where:

A = oven-dry weight of the test specimen before extraction, g,

B = oven-dry weight of the test specimen after extraction, g.

2. Alkali-reserve

The alkali-reserve is dependent on the presence in paper of materials such as calcium carbonate that are capable of absorbing acidic gases from the environment (ASTM 1992; ISO 1993).

Approximately 1 g of paper is weighed to the nearest 1 mg and is placed in approximately 25 ml of distilled water in a 250 ml conical flask. 20 ml of standardised 0.1 N HCl is pipetted into the flask, the solution is heated to boiling, and is then allowed to boil for approximately 1 minute. Three drops of aqueous methyl red are added. The solution is cooled to room temperature and is titrated to the first lemon yellow with standardised 0.1 N sodium hydroxide (NaOH) solution.

The alkali-reserve in the paper is calculated as moles per kilogram of paper.

$$\text{Alkali reserve(mol / kg)} = \frac{(ml \cdot N)\text{HCl} - (ml \cdot N)\text{NaOH}}{\text{DW}} \qquad (2)$$

where DW = dry weight of sample, g.

3. Ash content

This method is used to determine the amount of ash left when a paper is ignited. An estimate of the amount of inorganic material in the paper is thereby provided. The ash from paper may be derived from mineral matter in the pulp from which the paper was made, residues of chemicals used in its manufacture, extraneous mineral matter picked up during manufacture, and loading and coating materials (TAPPI 1985c).

1 g of paper is weighed in a dry silica crucible and placed in an oven at 800°C. After 3 hours, the crucible is removed, placed in a desiccator and weighed when it has cooled to room temperature. The ash content is calculated as:

$$\text{Ash content (\%)} = \frac{A}{B} \cdot 100 \qquad (3)$$

Where:

A = weight of ash, g,

B = weight of test specimen, moisture-free, g.

The filler content in paper may be calculated from the ash content if the material loss from the filler is known. For a kaolin clay, the loss on ignition is typically 12–13%, depending on the exact chemical composition.

4. Conductivity

The total water-soluble ionic substance is found by measurement of the conductivity of the water extract (Skoog 1985). Air-dried cut paper (1.0 g) is weighed into a 100 ml beaker. Distilled water (approx. 20 ml) is added and the paper is macerated with a stirring rod until it is uniformly wetted. Additional water (50 ml) is added, the mixture is stirred well, and the beaker is covered with a watch glass. After 1 hour, the mixture is stirred again and (without filtration) the conductivity is measured with a conductivity meter.

5. Copper number

The copper number is a measure of reducing groups in cellulose. In native cellulose, the only important reducing group is the terminal glucose unit of the long chain, and the copper number is very low. Oxidation and hydrolysis result in a larger content of reducing, chiefly carbonyl, groups (Browning 1977; TAPPI 1988d).

Two methods are used, depending of the value of the copper number (<1 or >1).

The paper is disintegrated in a grinder. Just before use, a 100 g/l copper II sulphate solution (A) and a solution (B) containing 350 g/l sodium carbonate and 50 g/l potassium carbonate are prepared. The sample (2.5 grams) is weighed and placed in an Erlenmeyer flask with 100 ml of boiling solution containing 5 ml of A and 95 ml of B. At the same time, samples for moisture determination are weighed. The flask is covered with a watch glass, submerged in a steam bath and maintained at 100°C for 3 hours.

After 3 hours, the flask is removed from the bath and the content is filtered on a sintered glass filter No. 2 in a suction flask.

The fibres are washed by flooding them with the sodium carbonate solution (100 ml) and then with hot water (250 ml) at about 95°C.

The filtrates are discarded and the suction flask is rinsed with water. Molybdophosphoric acid solution (25 ml) is added to the fibres. After 20 minutes, the sample is filtered and washed in a suction flask with cold water until the blue molybdenum colour is removed from the fibres. The filtrate is titrated with a potassium permanganate solution (5%) to a faint pink colour.

The copper number is :

$$\mathrm{Cu\text{-}No.} = \frac{0.316 \cdot V}{E} \tag{4}$$

Where:

V = millilitres of $KMnO_4$ solution required for titration,

E = grams of sample taken after deduction of moisture content.

If the copper number is greater than 1, another method must be used:

1 gram of paper is placed in a beaker with 40 ml of a copper sulphate solution (65 g/l) and 20 ml of a potassium/sodium tartrate and sodium hydroxide solution (200 g/l of potassium/sodium tartrate; 150 g/l of NaOH). This mixture is boiled for exactly 3 minutes and then filtered, rinsed and titrated as in the normal method.

6. DP (Degree of Polymerisation from viscosity measurements)

This method is used to determine the degree of polymerisation of cellulose, often presented by abbreviation DPv. The viscosity is related to the chain length or molecular weight of the cellulose (Browning 1977; TAPPI 1985b).

Ground cellulose (0.05 g) and 45 ml of cupriethylenediamine are mixed in a flask. The mixture is shaken with small glass balls for 20 minutes. The viscosity of the solution is then measured with a viscometer. 20 ml of the solution is placed in a viscometer of the "commission de la cellulose" type, AFNOR standard T12-005. This viscometer is placed in a thermostated bath (20°C). The viscosity is measured by timing the drop in liquid level through a given calibrated distance. The value obtained depends on the viscosity of the solvent.

The viscosity ratio η_{rel} (relative viscosity) is then:

$$\eta_{rel} = \frac{\text{viscosity of solution}}{\text{viscosity of solvent}} = \frac{t}{t_0} \tag{5}$$

Where:

t = efflux time of the solution,

t_0 = efflux time of the solvent.

The limiting viscosity number $[\eta]$ (intrinsic viscosity) is defined by the expression:

$$[\eta] = \lim_{c \to 0} \frac{\eta_{rel} - 1}{c} \tag{6}$$

where, c is the concentration of the solution. The limiting viscosity number is generally calculated from Martin's formula:

$$\log \frac{\eta_{rel} - 1}{c} = \log[\eta] + k[\eta]c \tag{7}$$

where, in the present calculations, the value k=0.14 was used. The degree of polymerisation may be related to the limiting viscosity number through the Mark-Houwink equation:

$$[\eta] = Q \cdot DP^a \tag{8}$$

where the values $Q=7.5 \cdot 10^{-3}$ and $\alpha=1$ were used.

7. pH cold extract

This method is used to determine the hydrogen ion concentration of paper extracts (ISO 1981; TAPPI 1988e).

Air-dried cut paper (1.0 g) is weighed into a 100 ml beaker. Distilled water (approximately 20 ml) is added and the paper is macerated with a stirring rod until it is uniformly wetted. Additional water (50 ml) is added, the mixture is stirred well, and the beaker is covered with a watch glass. After 1 hour the mixture is stirred again and (without filtration) the pH is measured with a glass electrode pH meter.

8. TOC

This method is used to determine the content of total organic carbon in paper extracts (Sprokholt 1992).

Total organic carbon is determined by measuring the carbon dioxide released by chemical oxidation of the organic carbon in the sample. After the sample has been acidified and purged of the total inorganic carbon, sodium persulphate ($Na_2S_2O_8$), a strong oxidiser, is added. This oxidant quickly reacts with organic carbon in the sample at 100°C to form carbon dioxide. When the oxidation is complete, the carbon dioxide is purged from the solution, concentrated by trapping, and then desorbed and carried into a non-dispersive infrared analyser (NDIR) which has been calibrated to display directly the mass of carbon dioxide detected. The resulting mass of carbon in the form of carbon dioxide is equivalent to the mass of organic carbon originally in the sample.

Mechanical analyses

1. Folding endurance KM (Köhler-Molin)

This method is used to determine the folding endurance of paper. The principle of the method is that a narrow strip of paper is folded backwards and forwards in a standardized manner and is thus subjected to a longitudinal stress until it breaks (ISO 1978; SCAN 1977).

Folding endurance, is the logarithm (to the base 10) of the number of double folds required to cause rupture in a strip of paper 15 mm wide tested under standardised stress conditions.

2. Tear test

This method is used to determine the internal tearing resistance of paper.

The *internal tearing resistance* of paper is the energy required to complete the out-of-plane tearing of an initial cut divided by the tearing length. The tearing resistance is therefore expressed in J/m or N. If the initial slit is in the machine direction, the result is given as machine direction tearing resistance; and similarly for the cross direction (ISO 1985b; SCAN 1973).

The principle of the method is that an initial cut or cuts is/are made:

a) in several sheets simultaneously, or
b) in a single sheet of paper.

Several (normally four) sheets together, or the single sheet, are/is torn through a fixed distance using a pendulum to apply the tearing force. The work done in tearing the test piece is measured by the loss in potential energy of the pendulum. The scale is calibrated to indicate the average tearing force (work done divided by the total distance torn). The *tear index* of the paper is determined from the internal tearing resistance divided by the grammage and the number of sheets in the test piece (Nm^2/g or kJm/kg).

3. Tensile strength properties

The mechanical properties of paper are usually determined in the two principal directions, the machine direction MD, and the cross machine direction CD. From these values, the geometric mean is calculated according to the formula:

$$\text{Geometric Mean} = \sqrt{\text{Machine Direction} \cdot \text{Cross Machine Direction}} \tag{9}$$

The geometric mean value corresponds to an isotropic sheet and thus facilitates the comparison of sheets with different mechanical anisotropies. Therefore, in most of the graphs and tables of this report, the geometric mean value is used.

The term index is used in the paper industry to denote that a strength value has been normalised with respect to the grammage of the sheet. The tensile index, for example, is defined as the force (N) per unit width (m) per unit grammage (g/m^2) that a strip of paper withstands at break.

From the new standard SCAN-P 67:93 (SCAN 1994), we obtain the tensile index, strain at break, tensile energy absorption index and the tensile stiffness index. In this method, the test piece length is 100 mm and the rate of elongation is 1.7 mm/s. This strain rate is approximately ten times higher than that prescribed by earlier standards (ISO 1985a; SCAN 1980).

Tensile strength is the maximum tensile stress developed in a test specimen before rupture in a tensile test carried to rupture under prescribed conditions. Tensile strength is the force per unit width of test specimen. *Tensile index* is tensile strength normalised with respect to grammage.

Stretch at break is the maximum tensile strain developed in the test specimen before rupture in a tensile test carried to rupture under prescribed conditions. The strain (or percentage elongation) is expressed as a percentage, *i.e.* one hundred times the ratio of the increase in length of the test specimen to the original test length.

Tensile energy absorption (TEA) is the work done when a specimen is stressed to rupture in tension under prescribed conditions, as measured by the integral of the tensile stress over the range of tensile strain from zero to maximum strain. The TEA is expressed as energy per unit area (test span width) of the test specimen. *Tensile energy absorption index* is the TEA normalised with respect to grammage.

The *tensile stiffness index* is calculated from the steepest slope of the force–elongation curve.

4. Zero-span tensile strength

The zero-span tensile strength depends mainly on the fibre strength, and only to a minor degree on the bonding between the fibres (and other constituents of the sheet). This test is therefore used to monitor changes in the tensile strength of the fibres themselves.

This method is used to obtain a measure of the average ultimate strength of the longitudinal structure of individual fibres in a pulp test handsheet. An index of the cohesiveness of fibres in the sheet is also provided by the ratio of the normal to the zero-span tensile index of test sheets having randomly oriented fibres (TAPPI 1985a). The equipment used is for example of the Pulmac type (Cowan 1975).

The zero-span tensile strength is reported in N/m or as a *zero-span tensile index* kNm/kg, calculated from the average zero-span tensile strength divided by the grammage.

Physical analyses

1. Moisture content

This method is used to determine the amount of moisture in paper (TAPPI 1990).
2 g of paper is weighed into a dry weighing bottle and placed in an oven at a temperature of 105°C. After being heated for a suitable period, the paper is cooled in a desiccator and then weighed again. This procedure is repeated until a constant weight is reached.

$$\text{Moisture content (\%)} = \frac{A-B}{A} \cdot 100 \tag{10}$$

where:

A = weight of sample before drying, g,
B = weight of sample after drying, g.

2. Optical reflectance

The intrinsic optical properties of paper were determined with a Datacolor Elrepho 2000 reflectometer. With the Elrepho 2000, 16 reflectance values are obtained over the wavelength range 400–700 nm. Standardised optical properties are then computed automatically from the spectral data, *e.g.* opacity and Y-value (ISO 1977b), ISO brightness (ISO 1977a; SCAN 1993a), whiteness (SCAN 1993b), *etc.* Light scattering and light absorption coefficients may be calculated using the Kubelka-Munk theory (Van den Akker 1949) over the visible spectrum, as well as for certain filter combinations. By adjusting the UV-content of the illumination, the degree of fluorescence from optical brightening agents (OBA) may be determined (Bristow 1994).

References

ASTM (1992).
ASTM D 4988: Determination of alkalinity of paper as calcium carbonate (alkali-reserve of paper).

Bristow, J. A. (1994).
The calibration of instruments for the measurement of paper whiteness.
Color Research & Application, 6.

Browning, B. L. (1977).
Analysis of paper.
Marcel Dekker, New York.

Cowan, W. F. (1975).
Short span tensile analysis.
Pulmac Instruments Ltd., Montreal, Canada.

Havermans, J. B. G. A. (1991).
Onderzoek naar het karakteriseren van papier en papierveroudering met infrarood–onderzoek. PK 90.1118.
Centrum TNO Papier en Karton, Delft, The Netherlands.

ISO (1977a).
ISO 2470: Paper and board.
Measurement of diffuse blue reflectance factor (ISO brightness).

ISO (1977b).
ISO 2471: Paper and board.
Determination of opacity (paper backing). Diffuse reflectance method.

ISO (1978).
ISO 5626: Paper. Determination of folding endurance.

ISO (1981).
ISO 6588: Paper, board and pulps. Determination of pH of aqueous extracts.

ISO (1985a).
ISO 1924/2: Determination of tensile properties.

ISO (1985b).
ISO 1974: Paper. Determination of tearing resistance.

ISO (1993).
ISO/CD 10716: Paper and board. Determination of alkali reserve.

Kolseth, P.; M. L. Samuelsson (1995).
Accelerated ageing of paper. A critical review of methods and evaluation.
To be published.

SCAN (1973).
SCAN-P 11: Tearing resistance of paper and board.

SCAN (1977).
SCAN-P 17: Folding endurance. Köhler-Molin tester.

SCAN (1980).
SCAN-P 38: Tensile strength, stretch and tensile energy absorption.
Constant rate of elongation method.

SCAN (1993a).
SCAN-P 3: Pulps, paper and board. ISO brightness.

SCAN (1993b).
SCAN-P 66: Paper and board.
CIE-Whiteness (D65/10°).

SCAN (1994).
CAN-P 67: Pulps, papers and boards. Tensile strength, strain at break, tensile energy absorption and tensile stiffness.
Constant rate of elongation method (1,7 mm/s).

Skoog, D. A. (1985).
Principles of Instrumental Analysis.
Saunders College Publishing.

Sprokholt, R. P. A. (1992).
Het meten van de totale hoeveelheid opgelost en colloidaal organisch en anorganisch koolstof in de waterfase met behulp van de TOC-analyzer.
Centrum TNO Papier en Karton.

TAPPI (1985a).
TAPPI T 231: Zero-span breaking length of pulp.

TAPPI (1985b).
TAPPI T 254: Cupriethylenediamine disperse viscosity of pulp (falling ball method).

TAPPI (1985c).
TAPPI T 413: Ash in paper and paperboard.

TAPPI (1988a).
TAPPI T 212: One percent sodium hydroxide solubility of wood and pulp.

TAPPI (1988b).
TAPPI T 266: Determination of sodium, calcium, copper, iron, and manganese in pulp and paper by atomic absorption spectroscopy.

TAPPI (1988c).
TAPPI T 401 om-88: Fiber analysis of paper and paperboard.

TAPPI (1988d).
TAPPI T 430: Copper number of pulp, paper, and paperboard.

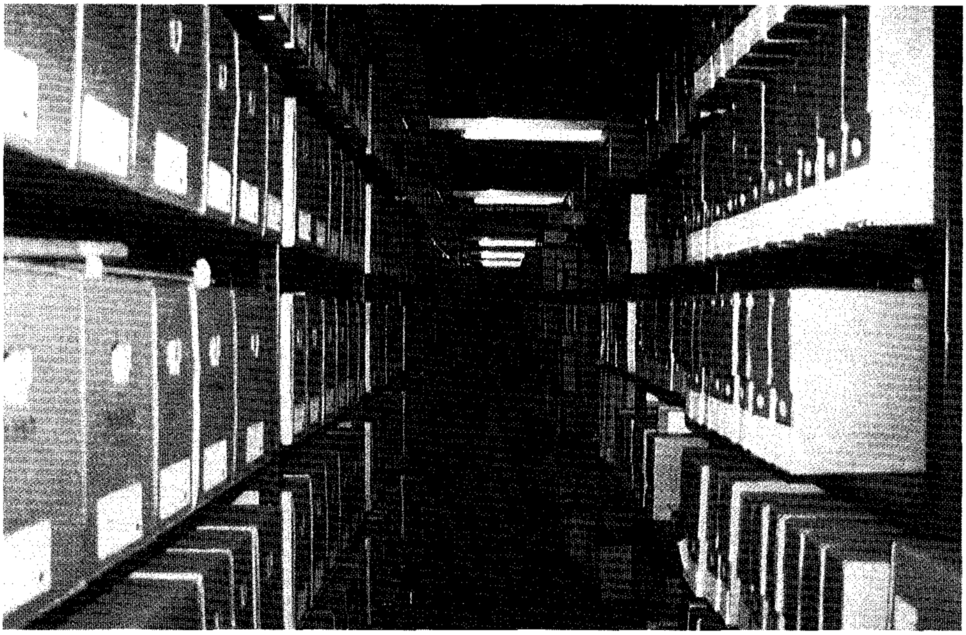
TAPPI (1988e).
TAPPI T 509: Hydrogen ion concentration (pH) of paper extracts (cold extraction method).

TAPPI (1990).
TAPPI T 412: Moisture in paper and paperboard.

Van den Akker, J. A. (1949).
Scattering and absorption of light in paper and other diffusing media.
Tappi 32 Journal 32: 498–501.

Willis, K. A.; J. H. v. d. Maas; R. G. J. Miller (1987).
Laboratory methods in vibrational spectroscopy.
John Wiley & Sons.

SUMMARY
(SAMENVATTING)



Environmental Influences on the Deterioration of Paper

SUMMARY

Sometimes in this modern era of digitised information, it is forgotten that one of the oldest and most used media is paper. The long-term storage of paper records is not *per se* the main purpose of archives, libraries and museums, but rather to provide accessibility to the printed or written records. In this thesis, the effects of several environmental conditions on the accelerated deterioration of paper are described aiming at contributing to the extension of the lifespan of paper.

The deterioration of books and archive materials due to acidification became apparent at the beginning of this century, but research to investigate the reasons for this and to develop preservation possibilities started only some decades ago. Two research programmes within this area deserve to be mentioned here: the Dutch ACBAM[1] project and the Swedish R&D project[2] on paper preservation. Both research teams have co-operated within the European R&D programme STEP[3].

Chapter 1 of this thesis presents a theoretical introduction to the problem of paper deterioration related to the history of papermaking and contaminants present in the air, and also the seasonal dependence of the concentration of air pollutants. A model using certain levels of pollutants in deterioration studies is given, concluding with a proposal for the use of the ratio $SO_2 : NO_x = 1 : 2$ in artificial deterioration studies.

As the performance of paper cannot be directly measured, it must generally be related to the results of chemical or physical test methods. Therefore an analytical tool for the characterisation of paper and paper ageing is described in **Chapter 2**: Fourier Transform Infrared Spectroscopy (FTIR). Commercial cellulose and lignin samples were analysed. Besides the bleached softwood cellulose used, papersheets were made and exposed to 50±5 ppm sulphur dioxide for 8 weeks in a stainless steel cabinet to determine the effects of SO_2 on the accelerated ageing only. It was concluded the crystallinity index calculated from FTIR spectra is a useful tool for determining paper acidification. It was also concluded that

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[1] ACBAM stands for the Dutch research programme: "de mate van Aantasting van Cellulose en lignine bevattende materialen in relatie tot de concentraties van luchtverontreinigende verbindingen in Nederlandse Bibliotheken, Archieven en Musea"

[2] Official name is FoU-Projektet för Papperskonservering

[3] STEP stands for Science and Technology for Environmental Protection, and is a framework programme of the European Community, Directorate General XII for Science Research and Development

cellulose exposed to SO_2 forms hydrocellulose, which has a higher reducing power in a (boiled) solution than cellulose in its solid state.
Infrared spectroscopy provides an important contribution to the characterisation of the morphology of cellulose. Lignin can be detected and also lignin of different origin, *i.e.* hardwood and softwood lignin, can be distinguished at levels where normal microscopic fibre determinations are inadequate. Furthermore hemicellulose present in wood cellulose can be detected.

The natural ageing of paper was investigated using naturally aged paper obtained from the National Library in The Hague and this is described in **chapter 3**. The paper used consisted of sheets from the book "Land om Land" by G.B.J. Hilterman, published by NV Uitgeversmaatschappij Elsevier, Amsterdam (1945). The copy used was originally stored at the New York Public Library (USA). Infrared spectroscopy showed that the crystallinity of the centre of the sheet is much higher than that of the margin and that, due to ageing, the centre of the sheets also contains more ester groups than the margin, probably a lignin-polysaccharide complex. Furthermore, it was concluded that hornification plays a role in the ageing of the book, possibly due to unsuitable storage conditions (hot and dry).

Since oxygen plays a role in the oxidative deterioration of paper, the ageing during storage of paper in normal and in inert environments was studied. Different paper grades were exposed to various climatic conditions; an inert gas (argon) and oxygen-rich and oxygen-depleted environments, as described in **chapter 4**. The results of the study demonstrated that the extent of thermal degradation is reduced when the oxygen concentration in the atmosphere is reduced. Besides, it was found that thermal ageing using dry heat only, as described in the standard method ISO 5630/1, causes hornification.

Chapter 5 describes the accelerated deterioration of paper using artificial pollution and thermal ageing experiments. Exposure to 10 ppm SO_2 and 20 ppm NO_x for 4 days at 23°C and 50% relative humidity (RH) was used, while thermal ageing is carried out for 12 days at 90°C and 50% RH. It was concluded that there was an increase in the accelerated ageing of paper in the presence of air pollutants. Also it was found that the deterioration during the thermal ageing differs from that in the presence of air pollutants. Besides, alkaline papers showed the absorption of NO_x with the formation of nitrates.

To prevent paper acidification or to protect paper from the acid contaminants, paper deacidification is often recommended. **Chapter 6** describes the positive effects of deacidification of archival materials using *DiEthylZinc (DEZ)*. It was concluded that the reproducibility of the DEZ-treatment was very good and that an effective amount of alkaline compounds was introduced into the paper. A homogeneous deacidification occurred with the DEZ-process and the treatment protects deacidified archive papers towards air pollutants like SO_2 and NO_2. The amount of alkaline compounds present, called the alkali-reserve, can be seen as the most important factor for the protection of the paper against acid attack.

Invloeden van het millieu op de veroudering van papier

SAMENVATTING

In het hedendaags tijdperk van gedigitaliseerde informatieoverdracht wordt weleens vergeten, dat papier behoort tot een van de oudste en meest gebruikte mediadragers. Het opslaan van papier in archieven en bibliotheken is geen doel op zich, maar een middel om de papieren documenten en boeken voor vele generaties raadpleegbaar te maken. Dit proefschrift beschrijft enkele milieu invloeden op de versnelde veroudering van papier met als doel een bijdrage te leveren aan de verlenging van de levensduur van ons papieren culturele erfgoed.

Het verval van boeken en archiefdocumenten ten gevolge van verzuring werd reeds in het begin van deze eeuw waargenomen. Echter onderzoek naar de oorzaken hiervan, mede gericht op het tegengaan van verval is pas de laatste decennia op gang gekomen. Een tweetal onderzoekprogramma's op dit terrein dat zeker het noemen waard is, zijn het Nederlandse ACBAM[1] onderzoek en het Zweedse R&D[2] onderzoek naar papierpreservering. Beide onderzoekteams hebben in 1991 in het Europese STEP[3] onderzoek samengewerkt.

Hoofdstuk 1 van dit proefschrift beschrijft de theoretische achtergronden van het werk, dat in dit proefschrift wordt weergegeven, in relatie tot de geschiedenis van het papiermaken en tot luchtverontreinigingen. Als conclusie wordt een model besproken van de verhouding van twee soorten luchtverontreiniging. Geconcludeerd wordt dat de verhouding $SO_2 : NO_x = 1 : 2$ overeenkomt met zowel de binnenlucht- als de buitenlucht-verhouding van beide verbindingen en toegepast kan worden voor experimenteel werk.

De gebruikerseigenschappen van papier kunnen niet direct worden gemeten, maar worden gerelateerd aan de resultaten van chemische en fysische metingen. Daarom worden in **hoofdstuk 2** analytische toepassingen van Fourier Transform Infrarood Spectroscopie (FTIR) beschreven. Commercieel verkrijgbare cellulose- en ligninepreparaten werden geanalyseerd. Daarnaast werden handmatig vellen papier gemaakt van gebleekte naald-

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[1] ACBAM staat voor: "de mate van Aantasting van Cellulose en lignine bevattende materialen in relatie tot de concentraties van luchtverontreinigende verbindingen in Nederlandse Bibliotheken, Archieven en Musea"

[2] Officiële benaming: FoU-Projektet för Papperskonservering

[3] STEP betekent Science and Technology for Environmental Protection, en is een framework programma van de Europese Gemeenschap, Directoraat Generaal XII voor Wetenschap, Onderzoek en Ontwikkeling.

houtcellulose. Deze vellen werden gedurende 8 weken aan een concentratie van 50±5 ppm SO_2 blootgesteld. Geconcludeerd werd, dat de kristalliniteitsindex, berekend uit de infrarood (IR) spectra, een gereedschap kan zijn voor het aantonen van de verzuring van papier. Daarnaast werd geconcludeerd, dat het aan SO_2 blootgestelde naaldhoutcellulose hydrocellulose vormt, dat een groter reducerend vermogen heeft in een (hete) waterige oplossing dan als vaste stof. Met IR spectroscopie kunnen morfologische veranderingen van cellulose worden aangetoond kan er een onderscheid worden gemaakt tussen naald- en loofhoutlignine, en kan hemicellulose worden gedetecteerd.

Een toepassing van het bovenstaande wordt getoond met een studie aan natuurlijk verouderd papier, dat van de Koninklijke Bibliotheek te Den Haag werd verkregen (**Hoofdstuk 3**). Het betrof monsters papier, afkomstig van bladzijden uit het boek "Land om Land" geschreven door G.B.J. Hilterman, en gepubliceerd door NV Uitgeversmaatschappij Elsevier, Amsterdam (1945). Het gebruikte exemplaar was oorspronkelijk afkomstig uit "the New York Public Library" (USA). Infrarood spectroscopie toonde, dat de kristalliniteit van monsters genomen uit het midden van de bladzijden hoger was dan die van de marge van de bladzijden. Tevens werd aangetoond, dat door de verschillende mate van veroudering in beide locaties er in het midden van de pagina's meer estergroepen voorkwamen, dan in de marge. Deze esters zijn mogelijk een lignine-polysaccharide combinatie. Verder werd aangetoond, dat verhoorning van cellulose een belangrijke rol speelt in de mate van veroudering van de bladzijden. Verhoorning van cellulose wordt beschreven als een afname van de reversibiliteit van de opname/afgifte van water, door een morfologische struktuurverandering. Dit door de slechte opslagomstandigheden waarin het boek heeft verkeerd.

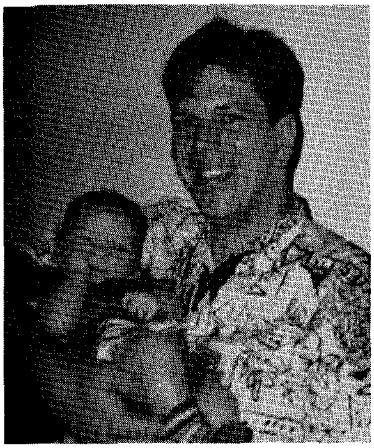
Het effect van papieropslag in een inerte atmosfeer wordt in **hoofdstuk 4** beschreven om na te gaan, welke bijdrage de oxydatieve afbraak van papier levert aan de totale veroudering. Verschillende papiersoorten werden bij 105 °C aan verschillende klimatologische omstandigheden blootgesteld. Toegepast werden o.a. een inert gas (argon) en een zuurstof-rijk milieu. Aangetoond werd, dat de thermische afbraak in een inerte atmosfeer wordt vertraagd. Daanaast werd aangetoond, dat ook thermische veroudering (3 dagen bij 105 °C, volgens de ISO standaard methode 5630/1) verhoorning van cellulose veroorzaakt.

Hoofdstuk 5 beschrijft de versnelde veroudering van papier met gebruikmaking van een kunstmatige blootstelling aan luchtverontreinigingen en een thermische verouderingsmethode. Verzuringsexperimenten werden uitgevoerd door o.a. papier 4 dagen bij 23 °C en 50% relatieve vochtigheid (RV) bloot te stellen aan 10 ppm SO_2 en 20 ppm NO_x terwijl de thermische veroudering plaatsvond door de papieren gedurende 12 dagen bloot te stellen aan 90 °C en 50% RV. Geconcludeerd werd, dat bij de aanwezigheid van de toegepaste luchtverontreinigingen de mate van veroudering wordt versneld. Bovendien bleek, dat er een verschil bestaat in het verouderingsmechanisme tussen het blootstellen aan de luchtverontreinigingen enerzijds en de thermische veroudering anderzijds. Nitraatvorming werd bij de toegepaste alkalische papieren waargenomen. Deze alkalische papieren bleken beduidend meer resistent te zijn tegen luchtverontreiniging dan de toegepaste zure en/of neutrale papieren.

Om de verzuring van papier tegen te gaan of om papier tegen verzurende verontreinigingen te beschermen, wordt veelal het ontzuren van papier aanbevolen. **Hoofdstuk 6,** tenslotte, beschrijft het effect van het ontzuren van papier met *DiEthylZink gas (DEZ)*. Geconcludeerd werd, dat de reproduceerbaarheid van het ontzuren met DEZ goed was, en dat er een effectieve hoeveelheid alkalische stof in het paper werd gebracht. Er trad een homogene ontzuring van het papier op en er werd een beschermende werking teweeg gebracht tegen luchtverontreinigingen als SO_2 en NO_2. De overmaat van ingebrachte alkalische verbindingen, de alkalische reserve, kan worden beschouwd als de belangrijkste preventieve factor tegen papierverzuring.

CURRICULUM VITAE

CURRICULUM VITAE



John Havermans was born on June 15th, 1956 in Schiedam, The Netherlands. He received his B.Sc. in organic chemistry in 1977 and his M.Sc. in Analytical Chemistry in 1990. In 1981 he started to work at the Timber Research Institute at TNO where he became projectleader on environmental chemistry and wood conservation. Since 1986 he was involved in the Dutch research programme on paper deterioration by air pollutants. In 1990 he started working at the TNO Paper and Board Research Institute with the primary task the scientifically co-ordination of the European STEP research project. In 1994 he was the local organiser of the First European Conference on Conservation of the European Cultural Heritage which was held in Delft, The Netherlands. Lectures were given not only at the University of Delft, but also for example at the ARSAG Conference (Paris, 1994), at the ASTM workshop (Philadelphia, 1994) and at the ICOM interim conference (Amsterdam, 1995).

CURRICULUM VITAE

John Havermans werd geboren op 15 juni 1956 te Schiedam. Hij behaalde het HBO-B diploma in de organische chemie in 1977 aan het Van 't Hoff Instituut te Rotterdam en in 1990 het doctoraaldiploma Scheikunde aan de RijksUniversiteit Utrecht met als hoofdvak Analytische Chemie en als keuzevakken Chemische Informatica, Polymeerchemie en Wetenschap & Samenleving.

Hij trad in 1981 in dienst van het voormalig Houtinstituut van TNO waar projectmatig werd gewerkt aan o.a. het meten van de formaldehyd-emissie uit plaatmaterialen. Vervolgens werd de functie van projectleider vervuld op het gebied van milieu en houtverduurzaming. De auteur werkt sinds 1986 mee aan het Nederlands meerjaren programma naar de mate van aantasting van cellulosehoudende materialen door luchtverontreinigingen, beter bekend als het ACBAM project, dat door het voormalig ministerie van Welzijn, Volksgezondheid en Cultuur werd gefinancierd. In 1990 aanvaardde hij tevens voor 2 jaar de functie van voorzitter van een werkgroep binnen de commissie van Europese standaardisering (CEN). Hij trad in 1990 in dienst van TNO Papier en Karton met als hoofdtaak het wetenschappelijk coördineren van het Europees STEP-onderzoek naar de invloeden van luchtverontreinigingen op de versnelde degradatie van papier. In 1991 werd hij werkgroepleider van de groep Papier, Produkt en Preservering. Hij organiseerde in juni 1994 "The First European Conference on Conservation of the European Cultural Heritage". Hij verzorgde tevens gastcolleges voor de VAPA-opleidingen en de TU-Delft. Presentaties werden gegeven voor o.a. de ARSAG Conferentie (Parijs, 1994); de ASTM workshop (Philadelphia, 1994) en de ICOM interim conferentie (Amsterdam, 1995). De auteur is sinds juli 1994 werkzaam binnen de groep Milieu en Duurzaamheid van TNO-KRI/BC als projectmanager.

EXPRESSION OF THANKS
(DANKWOORD)

EXPRESSION OF THANKS

Hereby I want to thank all, who helped to finish this work. Especially the Dutch Organisation of Applied Scientifically Research (TNO). Extra expression of thanks goes to prof.dr.ir. Herman van Bekkum, prof.dr.ir. Jan van Turnhout, Ronald van Deventer and Robert van Dongen. Also I want to thank the following institutes: Centre de Recherches sur la Conservation des Documents Graphiques, Göteborg University and Swedish Pulp and Paper Research Institute. The English editing was done by dr. J. Anthony Bristow which was very appreciated. Finally I want to thank my wife Gerarda for her love and inspiration.

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Eén van de weergegeven hoofdstukken behoorde tot een Europees Onderzoek en ik wil tevens via deze weg de drie betrokken instituten mijn dank betuigen voor het werk dat zij hebben verricht: Centre de Recherches sur la Conservation des Documents Graphiques, Parijs (Frankrijk), Göteborg University (Zweden) en Swedish Pulp and Paper Research Institute, Stockholm (Zweden).

Veel dank gaat uit naar Ronald van Deventer en Rob van Dongen van TNO.

De Engelstalige revisie werd verzorgd door dr. J. Anthony Bristow; een leerzaam proces, waarvoor ik hem zeer erkentelijk ben.

De totstandkoming van dit proefschrift zou onmogelijk zijn geweest zonder de inspiratie die mijn vrouw, Gerarda, mij heeft gegeven.